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SOIL SCIENCE

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Contents

The Absorption of Iron by Soils. H. C. Doyne and C. G. T. Morison.... 163

The Influence of Calcium and Nitrogen on the Protein Content of the Soybean Plant. Joseph M. Ginsburg and John W. Shive..... 175

Some Observations Upon the Effect of the Size of the Container Upon the Capillary Rise of Water Through Soil Columns. H. A. Wadsworth and Alfred Smith..... 199

Review of German Literature on Soil Science and Plant Physiology in 1925. 213

On the Origin and Nature of Soil Organic Matter or Soil "Humus": II. Method of Determining Humus in the Soil. Selman A. Waksman..... 221

The Relation of Light to Soil Moisture Phenomena. Leon B. Linford.... 233

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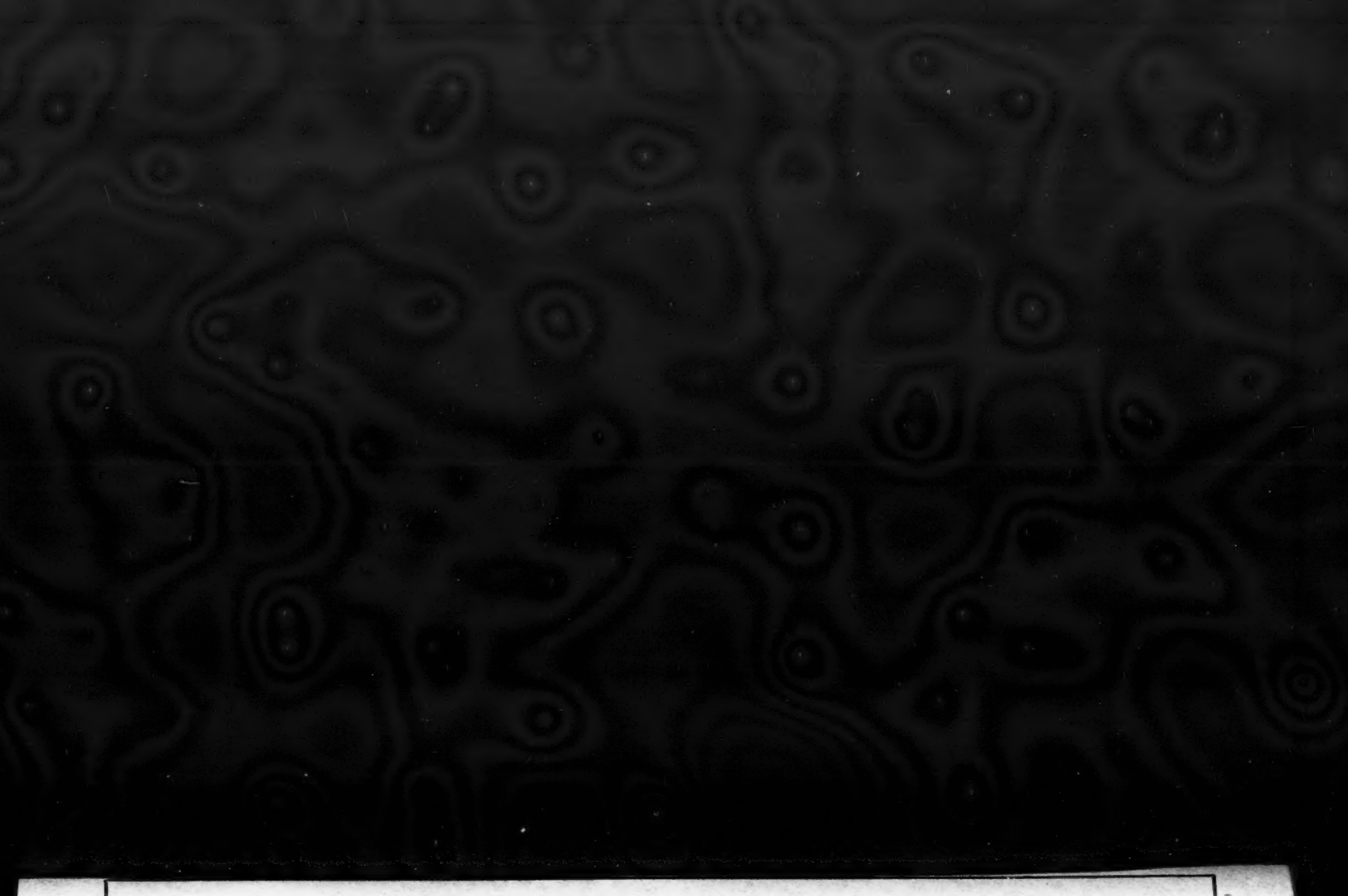

THE ABSORPTION OF IRON BY SOILS

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Iron is one of the elements which is present in soil in large quantities and is required by growing plants in almost infinitesimally small quantities.

It has long been known that solutions of ferrous salts are definitely toxic to plants, and that such solutions persist for only a very short time in normal soils, being oxidized with great rapidity and producing a harmless ferric salt which is retained. This retention is due to the fact that when a solution of a ferric salt is in contact with soil the iron is usually completely precipitated. This fact is made use of by Comber (1) in his method for distinguishing acid from neutral soils.

The work described in this paper was originally suggested by observations contained in a previous paper (2), which it was desired to investigate more fully. It has been shown by one of the authors (3) that it is not possible to distinguish with certainty the presence of ferrous compounds in soil, and that only when the concentration of the soil solution becomes abnormally low does there appear to be any movement of iron either in the form of a true solution or as a colloid sol. The object of the present work is to show: (*a*) the extent to which iron is removed from solution by various soils and (*b*) the soil constituents which are concerned in the removal.

In order to investigate the absorption of iron by various soils, 10 gm. of air-dried soil was placed in contact with 100 cc. of ferric chloride solution, containing 0.1482 gm. of iron. The mixture was kept in a flask and frequently shaken by hand for 15 hours. The contents of the flask were then filtered and the iron was determined in 25 cc. of the filtrate by a volumetric method which briefly consisted in:

(*a*) conversion into ions of any colloidal iron by boiling with a few cubic centimeters of concentrated sulphuric acid; (*b*) complete reduction of the iron from ferric to ferrous state by addition of a solution of stannous chloride; (*c*) removal of excess of stannous chloride by addition of concentrated mercuric chloride, which was reduced and precipitated as mercurous chloride; (*d*) determination of the amount of ferrous iron by titration with decinormal potassium bichromate using potassium ferricyanide as an external indicator.

The results of this experiment are given in table 1.

Of these soils there are three which show complete removal of iron from the solution used, and all of these contain considerable quantities of calcium carbonate, which would thus appear to be in part responsible.

TABLE 1

Absorption of iron from solution of ferric chloride by various soils

NUMBER	FORMATION	DISTRICT	TYPE OF SOIL	IRON ABSORBED BY 10 GM. SOIL
				per cent
C.	Kimeridge clay	Sandford, Oxon	Clay*	100.0
D.	Valley gravel	Oxford	Loam*	100.0
E.	Kimeridge clay	Sandford, Oxon	Clay*	100.0
P.	Alluvium	Otmoor, Oxon	Very heavy clay	71.5
Q.	Alluvium	Otmoor, Oxon	Very heavy clay, subsoil of P.	65.4
V.	Marlstone, Middle Lias	Adderbury, Oxon	Sandy loam,* high iron content	64.5
S.	Marlstone	Windrush Valley, Oxon	Sandy loam,* high iron content	58.8
R.	Marlstone	N. Oxon	Sandy loam, high iron content	56.9
L.	Calcareous grit	Fyfield, Berks.	Sand*	54.2
U.	Chalk	Assenden, Oxon	Sandy loam*	53.5
T.	Forest marble	Leafield, Oxon	Clay	50.4
B.	Kimeridge clay	Sandford, Oxon	Light clay	30.7
H.	Kimeridge clay	Bagley Wood, Berks.	Sandy clay subsoil	19.5
A.	Old red sandstone	Llanthoney, Monmouthshire	Sandy loam	9.2
G.	Plateau gravel	Tadley Common, Hants.	Sand	9.1
M.	L. greensand	Boar's Hill, Berks.	Sand	3.8
N.	Calcareous grit	Tubney, Berks.	Sand	4.6
O.	Calcareous grit	Tubney, Berks, subsoil	Sand, subsoil of N.	1.0

* No lime requirement.

Soils P and Q are from Otmoor, one of the heaviest soils in England, containing more than 40 per cent of clay but showing a positive lime requirement, and yet the absorption in this case is 71.5 for the surface and 65.4 for the subsoil.

The next group consists of three soils from the Middle Lias formation, containing very high amounts of iron. Only one of these soils shows a lime requirement, though all have a high iron absorption. The absorption in this case must be mainly due to something other than calcium carbonate.

Soils L and U show no lime requirement and contain appreciable quantities of calcium carbonate (0.25 per cent and 0.4 per cent respectively), and the remainder, all showing a positive lime requirement, have an iron absorption varying from 30 per cent in the case of clay soils to 1 per cent in the case of sands.

These results are sufficient to show that although calcium carbonate is an appreciable and important factor in the absorption of iron, other factors also contribute. There appear to be four such factors in soil: (*a*) calcium carbonate, (*b*) gross amount and activity of clay, (*c*) ferric oxide, (*d*) organic matter.

TABLE 2

Absorption of iron by soils at different depths

	$CaCO_3$	Fe REMOVED FROM 100 cc. 0.1 *N* $FeCl_3$ BY 10 GM. SOIL
	per cent	
First inch*	0.2508	56.3
Second inch	0.1672	54.2
Third inch	0.2090	54.2
Fourth inch	0.2132	54.2
Fifth inch	0.1923	53.5
Sixth inch	0.1044	50.0
Seventh inch	0.1754	50.0
Eighth inch	0.0334	43.6
Ninth inch	0.0417	40.2

* Top.

EFFECT OF CALCIUM CARBONATE ON IRON ABSORPTION

Additions of calcium carbonate to a solution of ferric chloride produce a change in colour of the solution from yellow to orange-brown, with evolution of carbon dioxide until there is sufficient calcium carbonate present to precipitate all the iron as ferric hydroxide, when the solution becomes completely free from iron. The change in colour is due to the formation of colloidal ferric hydroxide, which remains dispersed until the whole of the hydrochloric acid is removed, when it is precipitated as ordinary ferric hydroxide. The effect of calcium carbonate on iron absorption can be shown in the following experiments:

(*a*) In order to reduce the amount of calcium carbonate present 10 gm. of soil E was treated with 250 cc. of 0.5 *N* acetic acid and left to stand for 12 hours. The soil was then filtered and washed, transferred to a flask, and treated with 100 cc. 0.1 *N* ferric chloride solution. After the treated soil had been shaken at intervals for 16 hours, the amount of

iron absorbed was found to be 47 per cent whereas the original untreated soil absorbed 100 per cent. Presumably the removal of calcium carbonate by the acid treatment had some effect in lowering the iron-absorbing capacity of the soil.

(*b*) Soil U (poor arable field on chalk) was obtained in inch depths down to 9 inches. The calcium carbonate in each inch was determined by means of a Collins calcimeter, and the iron absorption of each inch was also determined.

Results are shown in table 2.

The percentage of iron removed is more uniform than would have been expected with the varying amounts of calcium carbonate, but there is no necessary uniformity in the other soil constituents, and doubtless the clay and humus play some part.

It is clear, however, that in the eighth and ninth inches where the calcium carbonate content is much decreased, iron absorption is also diminished.

Experiments by Comber (1) show that by treating a soil deficient in calcium carbonate with a solution of potassium thiocyanate a red colouration of ferric thiocyanate is observed. Presumably in the presence of calcium carbonate any iron replaced by potassium is immediately reprecipitated by the calcium carbonate.

EFFECT OF GROSS AMOUNT AND ACTIVITY OF CLAY ON IRON ABSORPTION

Soils P, Q, T, B, and H absorb respectively 71.5 per cent, 65.4 per cent, 30.7 per cent and 19.5 per cent of iron from solution. As all these show a positive lime requirement, the effect of calcium carbonate on the absorption of iron must be negligible. Presumably the colloidal clay content is the predominant factor, and the proportion of the clay fraction in these soils varies directly with their iron absorbing power, e.g., soil H is far the lightest and soils P and Q the heaviest, the latter containing over 40 per cent of clay.

Soil Q, which absorbs 65.4 per cent of iron from solution, was heated in a muffle furnace for 3 hours, after which, 10 gm. of the ignited soil was treated with 100 cc. of ferric chloride solution. Only 5.5 per cent of iron was removed from solution. The ignition of the clay soil destroyed its colloid constituents and consequently reduced its iron-absorbing powers.

The question remains as to whether the process is analogous to the absorption of exchangeable bases, or whether it is due to a mutual flocculation between the clay colloidal material and the colloidal ferric hydroxide that has been formed from the hydrolysis of ferric chloride. The following experiments may throw some light on this point:

Ten grams of soil Q, which shows a lime requirement of 0.1278 calcium carbonate, was shaken with 100 cc. of 0.1*N* hydrochloric acid. The mixture was filtered and 25 cc. of the filtrate titrated with 0.1*N* sodium hydroxide. The result showed that 42.2 per cent of the acid had been neutralized, presumably by the exchangeable bases in the soil.

It is reasonable to suppose that these exchangeable bases could remove some of the hydrochloric acid produced by hydrolysis of the ferric chloride, thereby

causing more ferric hydroxide to be formed, and that this ferric hydroxide would effect a mutual flocculation with the clay colloidal material, i.e., the balance of the equation would be shifted from left to right.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{(absorbed by clay)}}{Fe(OH)_3} + \underset{\text{(removed by exchangeable bases)}}{3HCl}$$

Comber[1] has shown that if a soil is treated with $2N$ hydrochloric acid its exchangeable bases will be removed and its powers of absorbing calcium from a solution of calcium bicarbonate will be considerably increased.

Soil Q was left in contact with $2N$ hydrochloric acid for 24 hours, subsequently was washed free of acid, and was air-dried. The soil was then shaken with ferric chloride solution as before, and it was found that 35.1 per cent of iron was absorbed, whereas the untreated soil absorbed 65.4 per cent of iron.

It may, therefore, be concluded that the absorption of iron by the clay fraction of a soil can be attributed chiefly to the effect of exchangeable bases in producing colloidal ferric hydroxide from the solution of ferric chloride by neutralizing the acid formed by hydrolysis, and that this ferric hydroxide effects a mutual flocculation with the clay.

EFFECT OF FERRIC OXIDE ON IRON ABSORPTION

The soils R, S, and V absorb respectively 56.9 per cent, 58.8 per cent, and 65.4 per cent of iron. These soils are very typical sandy loams, and, physically, they are not unlike soil A which absorbs 9.2 per cent of iron; consequently the clay fraction cannot contribute much to the absorption of iron. Their calcium carbonate content is below 0.1 per cent although R alone actually shows a lime requirement, so that calcium carbonate can be ruled out as an active factor in absorption. The predominating feature of these soils is their high iron content, which in terms of ferric oxide is: R, 26.5 per cent; S, 15.7 per cent; and V, 22.5 per cent. The iron in these soils may be in the form of a highly absorptive ferric hydroxide gel, which would appear to be the main factor in the absorption of iron. It is probable that the ferric hydroxide gel in these soils absorbs iron in the same manner as does the clay fraction. It was found that 10 gm. of soil R, which shows a lime requirement of 0.08134 per cent of calcium carbonate, neutralizes 51.2 per cent of $0.1N$ HCl, and that when "emptied" of its exchangeable bases by treatment with $2N$ hydrochloric acid, its iron absorbing powers are reduced from 56.9 per cent to 28.5 per cent.

[1] COMBER, N. M. Note on the absorption of calcium by soils. Paper read before the Conference of Advisory Agricultural Chemists (England). Department of Agriculture, the University, Leeds, England, October, 1924.

EFFECT OF ORGANIC MATTER ON IRON ABSORPTION

A further factor which must have some influence in iron absorption by a soil is its colloidal organic matter content. At the present stage this has not been investigated to any great extent.

An acid peat was found to absorb 32.6 per cent of iron; N, a sandy forest surface soil, absorbed 4.6 per cent, whereas its subsoil 0 absorbed 1 per cent. The difference between the heavy clay surface soil P and its subsoil Q is not relatively great, the amounts of iron absorbed being respectively 71.5 per cent and 65.4 per cent.

Probably partly because of the amount of exchangeable bases held, organic matter apparently does play a part in the absorption of iron. This point would be affected by the nature of the organic matter, the extent to which it has undergone decomposition, the rainfall of the district, and the permeability of the underlying soil.

It would appear, however, that each of the four constituents mentioned affect the removal of iron from solution. It should be borne in mind that the Comber method for the detection of acidity depends not only upon the absence of calcium carbonate, but also upon the absence, or comparative scarcity, of the three other constituents. In fact, soils Q and R show a lime requirement of 0.1278 per cent and 0.08134 per cent respectively, but give no red colouration with an alcoholic solution of potassium thiocyanate.

EFFECT OF INCREASING ADDITIONS OF CALCIUM CARBONATE ON THE IRON ABSORBING POWERS OF SOILS

As stated above, when small additions of calcium carbonate are added to a solution of ferric chloride, a sol of ferric hydroxide is produced which will ultimately be precipitated when sufficient calcium carbonate is present to neutralize all the hydrochloric acid produced on hydrolysis.

In the experiment, 9 flasks were each filled with 10 gm. of soil. To all but the first of these, calcium carbonate was added in regularly increasing amounts of from 0.05 to 4 gm. One hundred cubic centimeters of ferric chloride, containing 0.1482 gm. of iron, was added to the contents of each flask, which was corked up and shaken by hand at intervals for 16 hours. The corks were removed periodically to relieve the pressure caused by the evolution of carbon dioxide. The contents of the flask were then filtered and the amounts of iron in 25 cc. of the filtrate determined.

The results are given in table 3, and are shown graphically in figures 1 and 2. In the tabulation the second column shows the weight of iron present as colloidal ferric hydroxide which would be produced by that weight of calcium carbonate (in the first column) in accordance with the equation

$$3\,CaCO_3 + 2\,FeCl_3 + 3\,H_2O \rightarrow 3\,CaCl_2 + 2\,Fe(OH)_3 + 3\,CO_2$$

Actually no ferric hydroxide is precipitated by calcium carbonate alone until 0.4 gm. is added, which is sufficient to remove all the hydrochloric acid which can be produced by the hydrolysis of the ferric chloride.

TABLE 3

Iron absorbed by soils treated with calcium carbonate

$CaCO_3$ added	Fe as $Fe(OH)_3$ formed from $CaCO_3$	Fe absorbed by soil P	Fe absorbed by soil Q	Fe absorbed by soil QX	Fe absorbed by soil S	Fe absorbed by soil R	Fe absorbed by soil B	Fe absorbed by soil H	Fe absorbed by soil L	Fe absorbed by soil U	Fe absorbed by soil A	Fe absorbed by soil G	Fe absorbed by soil M	Fe absorbed by soil N	Fe absorbed by soil O
gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0	0	0.1060	0.097	0.052	0.085	0.080	0.0460	0.036	0.080	0.075	0.014	0.014	0.006	0.003	0.002
0.05	0.0186	0.1170	0.115	0.071	0.114	0.101	0.0626	0.047	0.091	0.097	0.028	0.036	0.031	0.022	0.025
0.10	0.0373	0.1360	0.131	0.080	0.133	0.117	0.0840	0.071	0.080	0.103	0.039	0.030	0.019	0.019	0.020
0.15	0.0559	0.1403	0.138	0.099	0.145	0.134	0.1090	0.087	0.080	0.107	0.047	0.032	0.016	0.022	0.018
0.20	0.0746	0.1450	0.146	0.117	0.148	0.140	0.1160	0.105	0.089	0.116	0.052	0.030	0.018	0.020	0.017
0.25	0.0932	0.1460	0.147	0.130	*	0.146	0.1230	0.121	*	0.116	0.052	0.030	0.018	0.024	0.017
0.30	0.112	0.1470	0.148	0.145	*	0.148	0.1370	0.134	*	0.116	0.052	0.028	0.018	0.024	0.017
0.35	0.1305	0.1480	0.148	0.148	*	*	0.1480	0.147	*	*	0.052	0.043	0.018	0.057	0.017
0.40	0.1492	*	*	*	*	*	*	*	*	*	*	*	*	*	*

* All iron removed.

Graphically the weights of iron absorbed by 10 gm. of soil are plotted against the weights of calcium carbonate added. On each graph, a "normal" is plotted

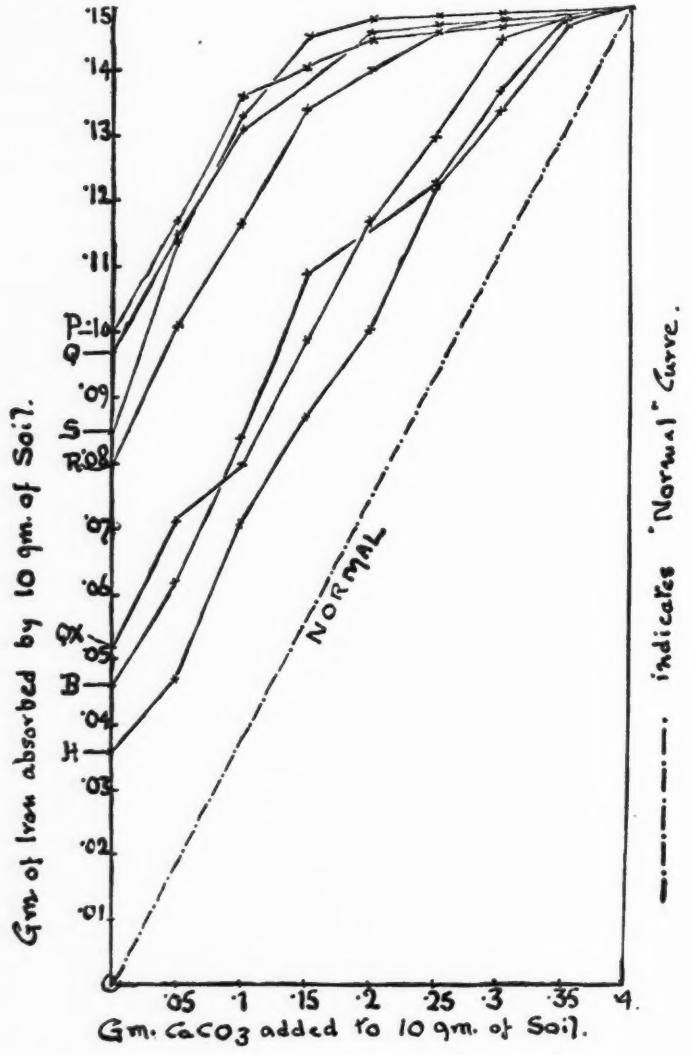

FIG. 1. BEHAVIOUR OF CLAYS AND SOILS WITH HIGH IRON CONTENT

resulting from the first and second columns in the table, i.e., the normal represents the iron as colloidal ferric hydroxide plotted against the weight of

calcium carbonate which would produce it. This curve will be referred to in future as the "normal."

Fig. 1 represents the behaviour of clay soils and soils with high iron content. In every case, no colloidal ferric hydroxide appeared in the filtrate and there was an increase in iron absorption as the weight of calcium carbonate was increased, so that as soon as any additional ferric hydroxide was formed, it was immediately removed by the colloidal material in the soil. Peculiar flocculation changes were also observed. On the addition of ferric chloride without calcium carbonate, the soil in the flask tended to flocculate. On increasing the quantities of added calcium carbonate, the soil suspensions became more and more turbid up to the point where all the iron was absorbed. At this point a very complete and extraordinarily rapid flocculation took place.

It will be further observed that in the soils P, Q, R, S, the curves are sensibly parallel to the "normal" curve, indicating that the colloidal ferric hydroxide, formed as a result of increasing additions of calcium carbonate, is absorbed by the soil.

The observed differences between the iron concentrations of the solutions in contact with the soil and containing no calcium carbonate, and that containing neither soil nor calcium carbonate, denote the original absorptive powers of the respective soils.

As the concentrations of iron in the solution diminish, the power of the soil to remove iron apparently decreases, and consequently over the latter portions of the curves the slope is more gradual.

The curves for the lighter clays B and H run practically parallel to the "normal" for their entire length, indicating that every successive amount of calcium carbonate is removed by the soil. This means that although the initial absorptive powers of the soils are less than in those discussed above, these powers are maintained over the whole range of concentrations in the experiments.

Soil Q, which gave a curve of the first class, was treated with cold 2*N* hydrochloric acid to remove the exchangeable bases; it was subsequently washed and air-dried, and its absorption determined.

The curve is shown under the heading QX and is seen to be one of the latter class, running roughly parallel to the normal for a considerable distance before it bends toward it, approaching the point where all the iron is absorbed.

The initial amount of iron absorbed where no calcium carbonate is added is also less than that of the untreated soil.

There is not sufficient evidence to determine whether these facts are entirely due to the removal of exchangeable bases. It is quite possible that the treatment with hydrochloric acid would effect some alteration in the soil colloids and that this is the responsible factor.

Figure 2 represents the behaviour of sandy loams and sands. The curves again fall under two heads. Those for the more loamy sands, A and U, gradually approach the normal, intersect it, and become horizontal before all the iron

is absorbed by excess of calcium carbonate. In other words, on the addition of calcium carbonate, absorption of iron by the soil was increased until all or nearly all the clay colloid in the soil was used up; after which, little or no ab-

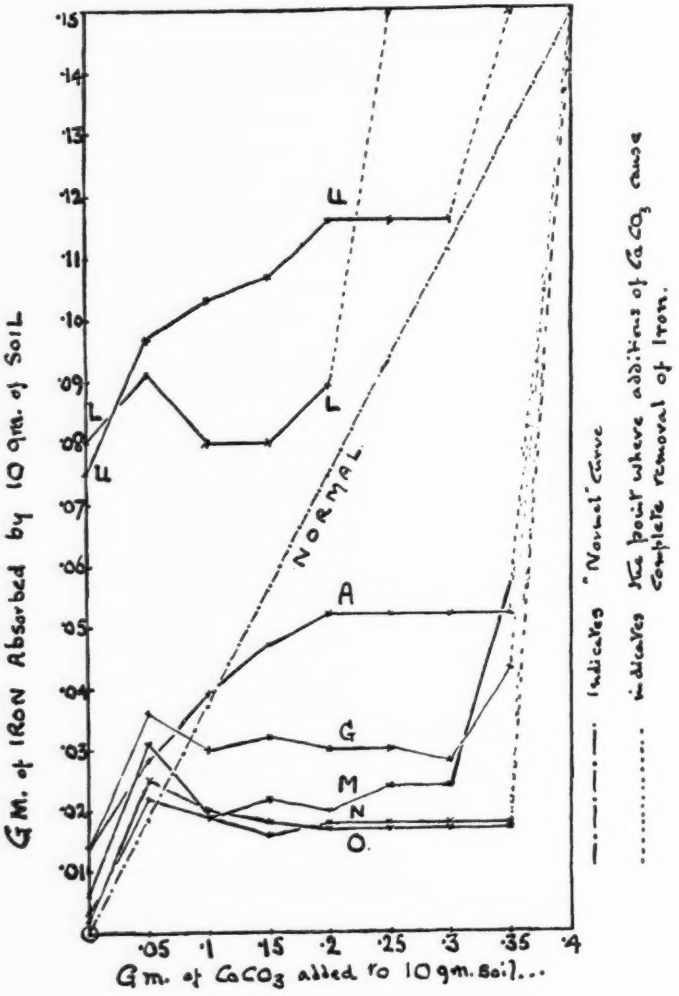

FIG. 2. BEHAVIOUR OF SANDY SOILS AND SANDS

sorption took place until sufficient calcium carbonate was added to precipitate all the iron, whether soil was present or not.

The flattening of the curve was always accompanied by the appearance of

the dark coloured iron sol in the filtrate, showing that the clay colloid in the soil had already been fully "saturated" with iron colloidal material.

It would appear that the maximum absorption of iron by a sandy loam which is deficient in calcium carbonate depends on its clay colloid content, and cannot be increased beyond this point by further additions of calcium carbonate until sufficient has been added completely to precipitate the iron.

Soils A and U behave in this way. It is interesting to observe that the calcium carbonate content of the soil itself has no effect on the type of curve produced when calcium carbonate is added; that is, soil U contains more calcium carbonate than soil A, which shows a lime requirement, and consequently the point where the curve for soil U starts is higher than the similar point for soil A, but the type of curve when further amounts of calcium carbonate are added is the same for both soils, and depends on the colloid content of the soil.

The second type of curve is typical for the behaviour of very coarse sands with the minimum amount of absorbent colloidal material. Such types of curves are represented by soils G, L, M, N, and O. Here again the calcium carbonate content of the soil affects only the starting point and not the type of the curve. (See curve for soil L.)

The curves themselves are peculiar: although the first addition of calcium carbonate raises the iron absorption, the second lowers it, and future additions produce a more or less horizontal curve, showing that no more iron is absorbed until sufficient calcium carbonate is added to precipitate the iron. The addition of 0.35 gm. of calcium carbonate usually had the effect of raising the iron absorption to some extent.

The first part of the curve is more or less parallel to "normal," showing that the absorption is proportional to the ferric hydroxide produced. A "kink" in the curve appears at this point. The "kink point" was always accompanied by intense turbidity and extremely slow filtration, although the soils were the coarsest of sands.

A possible explanation of this "kink point" is that a very thin coating of colloidal material, possibly silica, is held round the large sand particles. The first addition of calcium carbonate produced just sufficient ferric hydroxide to effect a mutual flocculation with all this colloidal material and draw it off the soil particles. Further additions of calcium carbonate produce more ferric hydroxide which would be sufficient to change the sign of the charge on this colloidal material and bring about a mutual *protection* of both colloids in place of a mutual *flocculation.*

It should be noted that similar curves for soil and subsoil are obtained in the case of soils N and O, indicating that the greater organic content of soil N, the surface soil, had little effect on the type of curve produced.

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THE INFLUENCE OF CALCIUM AND NITROGEN ON THE PROTEIN CONTENT OF THE SOYBEAN PLANT[1]

JOSEPH M. GINSBURG AND JOHN W. SHIVE

New Jersey Agricultural Experiment Station

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INTRODUCTION

Although the exact rôle that calcium plays in plant nutrition is not yet fully understood, it is becoming more and more evident that this element exerts a controlling influence on soil fertility. That its functions are manifold (30) has been well established by the numerous researches in modern agriculture. Russell (44) states that soils sufficiently supplied with $CaCO_3$ stand out in sharp contrast to those containing too little, although they may be otherwise of similar composition. The contributions of Gedroiz (9, 10) have brought out the dominant place that Ca takes in the colloidal complex in the soil. The remarkable antagonism of the Ca ion to the toxicity of other ions in plant growth, has been well demonstrated by Loeb (29), Osterhout (41), McCool (33), and Truog and Sykora (51). Truog (50) suggests that each species of plants has a certain lime-requirement which must be satisfied for maximum growth.

Indeed, the effect of $CaCO_3$ on the biological, chemical, and physical changes in the soil are known to the thoughtful farmer. Little is known, however, about the influence of calcium upon the biochemical activities within the plant itself, or concerning its intimate relation to other mineral nutrients in the metabolic processes of the plant. Recent experiments, carried out by several investigators, tend to indicate that a definite relationship exists between the amount of $CaCO_3$ in the soil and the nitrogen content of the plants grown in it. Especially is this true for legumes. But just what is the mechanism by which calcium increases the nitrogen content in plants is at present a matter of conjecture. Whether this phenomenon is brought about by direct action of the Ca ion within the plant, or indirectly by the effect of lime on the H-ion concentration of the soil solution, or by its beneficial influence on nitrogen fixation, our present knowledge concerning this subject is too scanty to warrant any definite conclusions.

Furthermore, the results obtained by different investigators in this field are not always in close agreement. Smith and Robinson (48) found that nodules on the roots of cowpeas and soybeans increased both the nitrogen and protein content of plants and seeds but did not increase the total yield. On the other hand Fred and Graul (8) report results which show that inoculation of soybeans increased the yield as well as the nitrogen content and that the yield was still further increased when supplemented by an application of lime. White (54) observed that the calcium content of clover and sorrel was highest where the maximum amount of limestone was applied and that both calcium and nitrogen were higher in the two crops when grown on a neutral or slightly alkaline soil than on an acid soil.

Results obtained by Lipman and Blair from a series of greenhouse and field experiments (22, 23, 24, 25, 26) show appreciable increases in the nitrogen content of soybeans, crimson clover, barley, vetch, and Canada field peas as a result of $CaCO_3$ applications to the soil.

[1] Paper No. 273 of the Journal Series, New Jersey Agricultural Experiment Station, Department of Plant Physiology.

The nitrogen in the legumes was higher with a liberal application of $CaCO_3$ than with a liberal application of $NaNO_3$. For a period of three years the percentage of nitrogen was higher in alfalfa hay from limed than from unlimed plots. Stalks, roots, and shelled beans of fourteen different varieties of soybeans grown on limed and unlimed soils were analyzed for total nitrogen. In each case, plants from limed plots were higher in this element and produced larger yields than those from the unlimed plots. Finally, the same authors conclude (27) from results of a ten-year period of crop rotation that the total yield in nitrogen was essentially the same for limed and unlimed sections where crop rotation without legumes was practiced; whereas in rotation with legumes, the plots where $CaCO_3$ or $MgCO_3$ was applied yielded distinctly larger crops and more total nitrogen than the unlimed plots.

Marked differences in the nitrogen content of red clover were also observed by Morse (35) in favor of the limed plots and were ascribed to higher nitrogen fixation brought about by the added $CaCO_3$. Alfalfa grown on soils ranging in pH from 3.0 to 7.1 was reported by Joffe (16) to increase gradually in nitrogen content with the corresponding decreases in H-ion concentrations. MacTaggart (32) concludes that, as a single element, nitrogen did not increase the nitrogen percentage of soybeans when applied to the soil in the form of dried blood. Experiments in culture solutions, carried out recently (12), have shown that in the absence of Mg, K, P, or Fe, soybean plants absorb low amounts of nitrogen and high amounts of calcium.

Parker and Truog (42), by comparing the composition of some thirty-four different species of plants taken from many different sources, found a direct relation between the nitrogen and calcium content. Higher calcium percentages were (with some exceptions) accompanied by a higher calcium-nitrogen ratio. They further advance the theory that the amount of calcium absorbed is proportional to the protein built up by the plants. Gile and Ageton (11) observed that $CaCO_3$ present in the soil in variations of from 5 per cent to 35 per cent had no effect on the amount of nitrogen fixed in the plants when bush beans, soybeans, radishes, sunflower, sugar cane, rice, and sweet cassava were grown. On the other hand, the soil high in $CaCO_3$ increased the calcium content only in soybeans, sugar cane, and sunflower. They also found that plants which were most depressed (rice and pineapple) showed the greatest increase in the amount of calcium. This last observation is in close harmony with that previously mentioned (12) although different plants were used.

Newton (39) grew peas, barley, and vetch in solutions low in calcium and found a corresponding decrease of this element in the plants, but no difference in the nitrogen content was observed. Furthermore, inoculated peas absorbed more nitrogen than the uninoculated when grown in solutions low in nitrogen, but did not absorb more calcium. That plants can take in large amounts of calcium without any injurious effects was also shown by Shedd (46). An increase of this element in legume plants occurred with the application of different calcium salts to the soil. This phenomenon, however, does not hold true for all plants and under all conditions. Bryan (4) found that a decrease in acidity from pH 5.0 produced a decrease in the calcium content of oats, but not of wheat plants. He also observed (3) that the greater the acidity of the culture medium, the less is the power of legume plants to obtain calcium for their metabolism.

Thus, all the experiments enumerated here, with only one exception, signify that the application of $CaCO_3$ to the soil increases the nitrogen content of plants. Discussion arises, however, whether this increased nitrogen is in protein form or merely as non-protein nitrogen. That this question is of practical importance from the standpoint of food value is obvious. Whereas an increase in protein means more food for human or animal consumption, a higher nitrogen content may not add anything to the food value of the crop. The term "protein" has been rather loosely used throughout the literature on this subject. Many authors speak freely of protein content in plants when only total nitrogen has been determined, overlooking the fact that the nitrogen percentage of the plant, especially of legumes, represents both protein and non-protein nitrogen.

The purpose of these experiments is, therefore, two-fold: First, to determine whether there exists a definite relation between calcium and nitrogen in plant metabolism. Secondly, to

ascertain whether the increased nitrogen found in plants as a result of lime application is in the form of protein or non-protein nitrogen. Solution cultures, in which the ionic concentration of the two elements under consideration can be approximately controlled, seemed to be best adapted to these studies. It was further thought that a comparison of solution-culture plants with those grown on soil submitted to a similar treatment might reveal some interesting correlations. The experimental data recorded in this paper represent, therefore, results secured from both solution culture and soil culture plants.

METHODS OF PROCEDURE

The plan of the experiments involved a study of the growth and composition of soybean plants (Manchu variety) grown in culture solutions containing varying proportions of calcium and nitrogen as well as in soil and in soil extracts with and without $CaCO_3$. Soybeans were selected because they are comparatively rich in both elements here considered. By employing soil extracts it was hoped to attain a culture medium in which the conditions for plant growth are more like those prevailing in the soil than could be possibly achieved in synthetic solutions. The entire investigation comprises four groups of plants according to the following treatments:

Group I. Culture solutions containing varying proportions of calcium and nitrogen in the form of $Ca(NO_3)_2$.

Group II. Culture solutions containing equal amounts of nitrogen and varying amounts of Ca as $CaCl_2$.

Group III. Soil extracts and culture solutions saturated with $CaCO_3$.

Group IV. Limed and unlimed soils.

The solution plants were grown in the greenhouse in two separate series, designated in the tables as *A* and *B* respectively. The second series was an exact duplicate of the first, but conducted at a different season of the year. In the first series, soybeans were grown from March 17 to August 25, whereas the second series was conducted from July 3 to September 5, 1924. The soil plants were grown during the summer months of the same year. When the plants had matured they were harvested and the dried material was analyzed for calcium, magnesium, protein nitrogen, and total nitrogen. Magnesium was determined with the object of studying the still debated question of the relation between the calcium and magnesium in plants (13, 19, 21 20, 31, 37). The determination of calcium, nitrogen and protein was required to carry out the purpose of the experiment.

For the culture solution work, a three-salt solution having an osmotic concentration of one atmosphere and containing the three salts KH_2PO_4, $Ca(NO_3)_2$, and $MgSO_4$ in volume—molecular concentrations of 0.0027, 0.0027, and 0.0161, respectively—was used as a check on the basis of which the other solutions were prepared. Two-quart glass jars were used for culture vessels and were arranged in the manner described by Shive (47) and Jones and Shive (18). Three plants were grown in each jar and duplicate jars were used, thus giving six plants for every solution in each of the two series. The solutions and the soil extracts were continuously renewed by means of a constant drip and drain

method (2) which allowed one liter of new solution to flow into each culture jar during a period of twenty-four hours while an equal amount of solution was automatically removed from each culture. Constant aeration was accomplished in the solutions by means of an air pump especially improvised for this purpose and described by Neller (38) and Allison (1).

Seeds, ranging in weight from 195 mgm. to 205 mgm. were germinated in sphagnum moss and seedlings of uniform size were transferred to the cultures. The culture solutions were prepared as used, from single 0.5 *M* stock solutions, and iron was added, whenever the plants appeared to require it, in the form of a freshly prepared solution of soluble ferric phosphate.

It was conceived from the very beginning that, if an adequate study of this problem is to be made, the composition of healthy plants only should be com-

TABLE 1

Osmotic concentrations, pH values, and salt concentrations (in grams per liter) of the culture solutions

GROUP	CULTURE NUMBER	pH VALUES	OSMOTIC CONCENTRATIONS	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$CaCl_2$	$CaCO_3$	TOTAL SALT CONCENTRATION
			atm.						
I	1	4.55	0.89	0.3715	0.2216	1.9261	.....	.....	2.5192
	2 (check)	4.54	1.00	0.3715	0.4430	1.9261	.....	.....	2.7406
	3	4.57	1.19	0.3715	0.8864	1.9261	.....	.....	3.1830
	4	4.58	1.57	0.3715	1.7728	1.9261	.....	.....	4.0694
	5	4.56	1.95	0.3715	2.658	1.9261	.....	.....	4.9558
II	6	4.48	1.18	0.3715	0.4430	1.9261	0.25	.....	2.9906
	7	4.47	1.35	0.3715	0.4430	1.9261	0.50	.....	3.2406
	8	4.39	1.68	0.3715	0.4430	1.9261	1.00	.....	3.7406
III	9	6.12	1.00	0.3715	0.4430	1.9261	.....	0.0420	2.7826
	10	4.50	.....	.....	.....	.....	.....	.....	0.3120
	11	6.28	.....	.....	.....	.....	.....	0.0375	0.3265

pared in order to avoid variations which may be brought about by some abnormalities in plant metabolism. Consequently, some preliminary work was carried out to test the effect on the growth of plants, of the culture solutions which were to be employed in this experiment.

The results of these preliminary tests showed that when calcium in the form of $Ca(NO_3)_2$ was present in solution in concentrations of 27 mgm. or less per liter, the plants grew poorly, showing chlorosis and hypertrophy near the base of the stem. On the other hand, when the amount of this salt in solution was increased to 864 mgm. or more of Ca per liter the plants exhibited considerable etiolation. Culture solutions containing 450 mgm. of Ca as $CaCl_2$ per liter produced plants with large leaf blades having a thin, glossy epidermis. Later the leaves became mottled with symptoms somewhat resembling those usually

observed in plants suffering from the mosaic diseases. On the basis of these results, the culture solutions were made up of such concentrations as to include the minimum and maximum amounts of calcium and nitrogen that proved efficient in producing normal plants.

Group I consisted of five cultures in which the calcium and nitrogen concentrations were varied in equal proportions by increasing or decreasing the amount of $Ca(NO_3)_2$ in the solution. Culture 2 was used as check, and cultures 1, 3, 4, and 5, contained one-half, two, four, and six times as much $Ca(NO_3)_2$ as did the check solution. The composition of the culture solutions, their osmotic concentrations, and their pH values are given in table 1.

In the cultures from group II, the concentration of nitrogen was exactly the same as that present in the check, but the calcium was increased to 198 mgm., 288 mgm., and 468 mgm. per liter in solutions 6, 7, and 8, respectively, by the addition of different amounts of $CaCl_2$. The osmotic concentration values of the culture solutions in the first two groups ranged from 0.89 to 1.94 atmospheres for the lowest and highest salt concentrations respectively. The distilled water employed for all the culture solutions was obtained from a Barnsted still.

The third group consisted of cultures, 9, 10, 11. Culture 9 had the same composition as that of the check with the exception that the distilled water used to make up this solution had been previously saturated with CO_2 and $CaCO_3$. The carbon dioxide was used to increase the solubility of calcium carbonate in solution. Cultures 10 and 11 consisted of soil extracts, the latter containing $CaCO_3$. Out of all the processes now in vogue for obtaining a soil solution (5, 6, 7, 14, 15, 34, 49, 52, 53), the water extraction method was chosen. The procedure in obtaining the extract was the same as that employed by the Bureau of Soils (45), except that the time of shaking, was 10 minutes instead of 3 minutes. The soil employed was a comparatively fertile Sassafras loam. Some difficulties were at first encountered in obtaining an extract free from colloidal material. The extracted solution remained turbid even after it was passed through a Pasteur-Chamberlain filter. It was, however, later discovered that a clear extract could be easily obtained when the pH of the soil (which was originally 4.92) was reduced to about 4.50. Evidently this pH corresponded to the isoelectric point of the soil colloids.

It was found by preliminary tests that by mixing the Sassafras loam with another soil which was still more acid, having a pH of 3.41, a mixture could be obtained, the reaction of which varied according to the proportions of the two soils used. Thus a mixture of one part of the very acid soil to eight parts of the Sassafras loam gave a water extract that ranged in pH from 4.46 to 4.54 as determined electrometrically from several extractions. This method was found more convenient and by far less time consuming than any one of the other methods tried in adjusting the reaction of the soil extract. The entire method briefly, consisted in shaking the mixture of the two soils for 10 minutes in five parts of water. The mixture was allowed to settle and the supernatant liquid filtered through a double filter paper.

The soil extracts thus obtained were comparatively rich in calcium and very poor in nitrogen. Four duplicate analyses of the extracts prepared at different times gave an average of 121 mgm. of calcium, 13 mgm. of magnesium, and only 7 mgm. of nitrogen per liter. For culture 11 the soil extract was first saturated with $CaCO_3$ and again filtered before it was transferred to the jars.

The initial H-ion concentrations were approximately the same for all the solutions except for those containing $CaCO_3$. The pH values, as shown in table 1, ranged from 4.39 in culture 8, to 4.58 in culture 4, as compared with 4.54 for the check solution. The $CaCO_3$ treatment lowered appreciably the H-ion concentration in the culture solution and in the soil extract, and the pH values for cultures 9 and 11 were 6.12 and 6.28 respectively.

The plants from group IV were grown in large galvanized iron tanks containing 100 pounds of soil. Mineral fertilizers in the form of 14 gm. of acid phosphate, 7 gm. of KCl, and 7 gm. of $NaNO_3$, were added to each tank, while $CaCO_3$ was added to two of the tanks only. The soil used here was the same as that from which the extracts were obtained for the cultures of the previous group. The addition of 136 gm. of $CaCO_3$ to each of the two tanks raised the pH of the soil from its original value of 4.92 to 6.70. The tanks were kept in the greenhouse and were watered frequently in order to maintain the moisture at about 50 per cent of the moisture holding capacity of the soil. Seeds taken from the same stock and of similar weight as those used for the solution cultures were planted on May 20. Twenty healthy seedlings were selected for each tank and were allowed to grow to maturity. The tops were harvested on August 22 and analyzed for the same constituents as were the plants from the solutions. In view of the fact that a large number of plants (forty) were harvested from the duplicate tanks for each treatment, it was not considered essential to repeat this part of the experiment as was done with the first three groups of plants.

The tops and roots were harvested separately from each culture and dried to constant weight at a temperature of 65°C. All the plant material from the corresponding cultures in each series was then combined, finely ground, and stored in tightly covered glass jars for chemical analysis. All the analyses were carried out in duplicate according to the Official Methods of the Association of Agricultural Chemists (40), and averages of the two determinations are presented in the tables. The calcium and magnesium were determined gravimetrically from the ash of the plants, while the protein was precipitated from the ground plant material and the nitrogen in the residue determined. For the total nitrogen determination the Kjeldahl method, modified to include nitrate nitrogen, was used.

EXPERIMENTAL RESULTS

Introductory

The results secured from each of the four groups of plants are presented in the succeeding tables separately and are then summarily discussed. The two different series of plants are designated *A* and *B* for the sake of clearness, and only one series of numbers (1 to 16) was employed to denote all the cultures of the different groups. The dry weights of tops and roots from the solution plants are given separately in tables 2, 4, and 6, and the chemical analyses of the same plants are shown in tables 3, 5, and 7. The data in table 8 represent both the dry weight and the composition of the tops from the soil plants. The appearance of the plants from groups I, II and IV are shown in plates 1, 2, and 3, respectively.

TABLE 2

Dry weights of plants grown in culture solutions of group I containing varying concentrations of calcium nitrate

CULTURE SOLUTIONS				DRY WEIGHTS								
	Milligrams per liter			Series A			Series B			Averages of Series A and B		
Culture number	$Ca(NO_3)_2$	Ca	N	Roots	Tops	Total*	Roots	Tops	Total*	Roots	Tops	Total
1	222	54	38	4.46	41.65	46.11	3.08	14.80	17.88	3.77	28.33	31.50
2 (check)	443	108	76	4.99	59.21	64.20	3.80	22.85	26.65	4.39	41.03	45.43
3	886	216	152	6.08	58.27	64.35	4.30	32.00	36.30	5.19	45.14	50.33
4	1,173	432	304	9.38	73.74	83.12	6.30	40.90	47.50	7.84	57.32	65.31
5	2,658	648	456	7.94	73.72	81.86	5.00	35.50	40.50	6.47	50.46	61.18

* Six plants.

Group I

An examination of the dry weights of the plants in group I (table 2) shows higher yields with increasing amounts of $Ca(NO_3)_2$ until the calcium concentration reaches 432 mgm. per liter of solution. With higher concentrations of this salt a decided decrease in the dry weights of roots in both series and in the dry weights of tops only in series B is noticed. Thus, solution 4 gave the highest total yield in both series, while the very luxuriant growth occurred in plants from both solutions 4 and 5, where the $Ca(NO_3)_2$ concentrations were highest, as may be clearly seen from plate 1.

The data from the chemical analyses presented in table 3 show a direct relation between the calcium content of the plants and the concentration of the same element in the solutions. The calcium content ranged from 0.55 per cent to 2.41 per cent in plants from the different cultures in series A and from 0.45 per cent to 2.44 per cent in those from series B. A clear generalization is here indicated. In each case a high calcium content in the plants corresponded to

a high concentration of this element in the culture solution, and a low calcium content in the plants corresponded to a low content of this element in the culture solution. This conclusion is perfectly definite for the conditions of this experiment, at least. On the other hand no such correlation was observed between the nitrogen content of the plants, either as total or as protein nitrogen, and the nitrogen content of the media. Although differences in the amount of nitrogen absorbed by the plants of the different cultures were observed, they were very slight and did not always correspond to the order of differences in the concentrations of this element in the culture solutions, and may not, therefore, be considered to have any significance in this connection. It is important to observe further that the same lack of relationship existing between the nitrogen content of the media and that of the plant is shown also for the calcium content of the media and the nitrogen content of the plants, since these

TABLE 3

Composition of plants grown in culture solutions of group I, containing varying concentrations of calcium nitrate

Culture number	CULTURE SOLUTION			COMPOSITION OF PLANTS											
	Milligrams per liter			Series A				Series B				Averages of Series A and B			
	$Ca(NO_3)_2$	Ca	N	Ca	Mg	Total N	Protein N	Ca	Mg	Total N	Protein N	Ca	Mg	Total N	Protein N
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	222	54	38	0.55	0.94	3.52	2.45	0.45	0.94	3.38	2.24	0.50	0.94	3.45	2.35
2 (check)	443	108	76	0.65	0.95	3.56	2.57	0.61	0.86	3.24	2.25	0.63	0.91	3.40	2.41
3	886	216	152	0.76	0.83	3.35	2.28	1.01	0.84	3.51	2.29	0.89	0.84	3.43	2.29
4	1,773	432	304	1.92	0.75	3.32	2.21	1.53	0.81	3.61	2.29	1.73	0.78	3.47	2.25
5	2,658	648	456	2.41	0.94	3.45	2.22	2.44	0.70	3.65	2.32	2.42	0.82	3.50	2.27

two elements varied in the culture solutions of this group in the same proportions. That is, variation in the calcium and nitrogen content of the culture media had no influence whatever on either the total nitrogen or the protein nitrogen of the plants. This is in direct variance with the definite relationship shown between calcium content of medium and of plant.

Comparing now the calcium and magnesium contents of plants and media it becomes obvious that a slight decrease of the latter occurred with considerable increase in the former. This relationship is quite definite for the culture of series B, but is not so definitely obvious for those of series A. Considering averages of the two series, however, the calcium content of the plants of the several cultures shows increasing percentage values ranging from 0.50 to 2.43 whereas magnesium shows a corresponding decrease in percentage values ranging from 0.94 to 0.78.

Group II

The cultures in group II differed from those in the previous one only in the source of calcium used; $CaCl_2$ instead of $Ca(NO_3)_2$, in successive increments of 0.25 gm., 0.50 gm., and 1 gm. per liter of solution was added to cultures 6, 7, and 8 respectively. Consequently the amount of nitrogen in each of the three cultures in this group remained unchanged from that initially present in the check solution; namely, 76 mgm. per liter.

TABLE 4

Dry weight of plants grown in culture solutions of group II treated with calcium chloride

CULTURE SOLUTIONS				DRY WEIGHTS								
Culture number	Milligrams per liter			Series A			Series B			Averages of Series A and B		
	$CaCl_2$ added	Ca	N	Roots	Tops	Total	Roots	Tops	Total	Roots	Tops	Total
6	250	198	76	5.38	44.92	50.31	4.50	27.00	31.50	4.94	35.96	40.90
7	500	288	76	5.15	51.34	56.49	4.95	42.10	47.05	5.05	46.72	51.77
8	1,000	468	76	6.64	51.94	58.58	5.30	44.70	50.00	5.97	48.32	54.29
Check	None	108	76	4.99	59.21	64.20	3.80	22.85	26.65	4.39	41.03	45.43

TABLE 5

Composition of plants grown in culture solutions of group II treated with calcium chloride

CULTURE NUMBER	CULTURE SOLUTIONS			COMPOSITION OF PLANTS											
	Milligrams per liter			Series A				Series B				Average of Series A and B			
	$CaCl_2$ added	Ca	N	Ca	Mg	Total N	Protein N	Ca	Mg	Total N	Protein N	Ca	Mg	Total N	Protein N
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
6	250	198	76	1.27	0.85	3.48	2.49	1.29	1.04	3.36	2.27	1.28	0.95	3.42	2.38
7	500	288	76	1.39	0.80	3.51	2.31	1.33	0.78	3.27	2.20	1.36	0.79	3.38	2.26
8	1,000	468	76	1.94	0.87	3.32	2.25	2.05	0.72	3.55	2.40	2.00	0.79	3.43	2.33
Check	None	108	76	0.65	0.95	3.56	2.57	0.61	0.86	3.24	2.25	0.63	0.91	3.40	2.41

In general the addition of $CaCl_2$ in the concentrations enumerated above did not exert any injurious influence on the growth of the plants. They appeared normal in every respect and produced good pods, as may be seen from plate 2 (showing photographs of the plants from series B) as well as from the dry weights given in table 4. Considering averages of the dry weights of tops from the two series, no marked benefits were derived from the addition of increasing increments of $CaCl_2$ to the culture solution. On the other hand, the dry weights of the roots were considerably higher in each of the three cultures than were those harvested from the check solutions, thus exhibiting

again, as has already been shown by the results from group I, the beneficial influence of the calcium addition on root development.

The data from the chemical analyses, given in table 5, show again a direct relation between the concentration of calcium in solution and the amount of this element absorbed by the plants, the relation being the same as that found in the plants of the preceding group. Plants from both series increased their calcium content with increasing amounts of $CaCl_2$ in the solution.

The percentages of the nitrogen varied somewhat, as is to be expected, but there is no correlation between nitrogen and the calcium content of the plants. This lack of correlation was also indicated for the plants of group I. Slight differences also occur in the protein-nitrogen content, but these differences are not significant and the protein-nitrogen appears to have no direct relation to either the calcium in the culture solution or in the plant.

TABLE 6

Dry weights of plants grown in culture solutions of group III and in soil extracts treated with calcium carbonate

CULTURE NUMBER	CULTURE SOLUTION			DRY WEIGHTS								
	Milligrams per liter			Series A			Series B			Average of Series A and B		
	$CaCO_3$ added	Ca	N	Roots	Tops	Total	Roots	Tops	Total	Roots	Tops	Total
9	42	1.25	76	4.94	44.67	49.61	2.85	23.10	25.95	3.89	33.84	37.78
10*	.....	1.21	7	7.08	37.08	44.16	.....	.....	.....	.....	.....	.....
11†	37	1.35	7	8.90	38.24	47.14	.....	.....	.....	.....	.....	.....
Check	None	1.08	76	4.99	59.21	64.20	3.80	22.85	26.65	4.39	41.03	45.43

* Soil extract.

† Soil extract and $CaCO_3$.

Appreciable differences in the magnesium content were observed in plants from series B, the percentage values of this element in the plants decreasing progressively with increasing values for calcium. Considering averages of the two series, this relation is more definitely shown for the cultures of this group than it is for the cultures of group I.

It may be of interest to note here that the plants grown in solutions containing high concentrations of $CaCl_2$ or $Ca(NO_3)_2$ notably cultures 4, 5, 7, 8, required considerably less iron to maintain the normal green color than did the plants grown in solutions low in concentrations of calcium.

Group III

Group III includes cultures 9, 10, 11. Culture 9 had exactly the same concentration of the three initial salts as had the check solution with the exception that the former was saturated with $CaCO_3$. Culture 10 represents the untreated soil extract, and culture 11 consists of the same soil extract treated with

$CaCO_3$. The numerical data concerning the dry weights and the chemical analyses of the plants of this group are given in tables 6 and 7.

The plants from culture 9 show an average total yield somewhat less than that from the check culture, but a marked increase is observed in the nitrogen content of these plants over those of the checks. The data of the chemical analyses show that the total nitrogen percentage (3.93 for series A and 3.81 for series B) for the two series was higher in these plants than in the plants from any of the cultures in the preceding groups. It is important to note that this superiority in nitrogen content is not manifested in the protein nitrogen of the plants. The percentage values of protein nitrogen found in the plants of the two series in question are not higher than those shown for the check plants or for the plants of any of the cultures of the preceding groups. The higher

TABLE 7

Composition of plants from group III grown in culture solutions and in soil extracts treated with calcium carbonate

CULTURE NUMBER	CULTURE SOLUTIONS			COMPOSITION OF PLANTS											
	Milligrams per liter			Series A				Series B				Average of Series A and B			
	$CaCO_3$ added	Ca	N	Ca	Mg	Total N	Protein N	Ca	Mg	Total N	Protein N	Ca	Mg	Total N	Protein N
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
9	42	1.25	76	0.79	0.84	3.93	2.40	1.19	0.84	3.81	2.25	0.99	0.84	3.87	2.33
10*	.....	1.21	7	1.02	0.46	1.51	1.42	....	....	....	....	....	....	....	....
11†	37	1.35	7	1.40	0.61	1.81	1.49	....	....	....	....	....	....	....	....
Check	None	1.08	76	0.65	0.95	3.57	2.57	0.61	0.86	3.24	2.25	0.63	0.91	3.40	2.41

* Soil extract.

† Soil extract and $CaCO_3$.

amount of nonprotein nitrogen found in these plants may be due to the fact that the initial H-ion concentration of this solution was considerably lower than that of the other cultures considered. This fact will be further emphasized in the following sections. The initial H-ion concentration of the culture corresponded to a pH value of 6.12 as compared with a pH of 4.54 of the check solution.

In the soil extracts the seedlings grew poorly during the first three weeks and showed characteristics usually exhibited by plants suffering from lack of nitrogen. During the fourth week, however, they began to show more vigorous growth, produced good leaves, and grew to maturity. This sudden change in the behavior of these plants was accompanied by vigorous nodule formation.

It may be of interest to mention here that practically all the nodules were formed on the base of the roots, that is, either entirely above or close to the

surface of the solution. Whether this was due to the greater abundance of oxygen on the surface, or to some inhibiting factor exerted by the solution, is at present not clear. It seems evident, however, that the reaction of the solution had no effect upon the process of symbiotic nitrogen fixation. The nodules were just as abundant on roots grown in the solution of culture 10 with a pH of 4.50 as they were on the roots of culture 11, in which the calcium carbonate lowered the initial H-ion concentration to 6.28.

Although no further nitrogen starvation was observed, the plants grown in the soil extracts never completely regained the rich green color which was displayed by the plants grown in the culture solutions. They were pale green throughout the growth period. It must be remembered here that the soil extracts used were very poor in nitrogen, containing only 7 mgm. per liter of extract.

It is regrettable that this part of the experiment could not be successfully repeated in the second series, as no nodules formed and the plants starved from lack of nitrogen and died after five weeks of scanty growth. The failure of the plants to form nodules may be explained, possibly, by the fact that the soil from which the extracts were made was kept in the greenhouse exposed to sunlight and may have become free from the symbiotic nitrogen-fixing bacteria by the time the second series was conducted. Inoculating the soil extract with a fresh culture of *B. radicicola* (soybean variety) when the plants had already reached an advanced stage of nitrogen starvation did not stimulate the roots to nodulation. These plants were discarded and the results from cultures 10 and 11 in series B are, therefore, not presented in the tables.

A comparison of the yields of the plants from the two soil extracts shows considerably higher dry weights of roots and only slightly higher dry weights of tops in favor of the $CaCO_3$ treatments. The application of $CaCO_3$ also increased both the calcium and the magnesium in the plants. Those from the untreated culture contained 1.02 per cent calcium and 0.46 per cent magnesium, whereas the plants from the treated culture showed corresponding values of 1.40 and 0.61, respectively.

The nitrogen content of these plants was considerably lower than in those from the culture solutions. Evidently the amount of nitrogen assimilated from the air by the symbiotic process was not sufficient to supply the plants' requirement. The plants from the soil extract to which $CaCO_3$ was added were appreciably higher in total nitrogen than were those from the untreated extract, but the percentage of protein nitrogen was approximately the same for both cultures. This higher total nitrogen content was here, as in culture 9, accompanied by a higher calcium content than is shown for the corresponding check cultures. Thus, in the two types of culture media here represented, the addition of calcium in the form of carbonate appreciably increased the total nitrogen of the plants but had no influence whatever on the protein nitrogen.

Group IV

Group IV, includes the plants from the limed and unlimed soils. Since duplicate tanks were used for each treatment, the dry weights, as well as the chemical analyses are given separately for each tank in table 8. The most significant influence of the $CaCO_3$ observed in this group was in the amount of dry weight produced by the plants. The total crop from tanks 13 and 14 was 62.55 gm., whereas 96.40 gm. were harvested from tanks 15 and 16, which received lime. These differences are clearly brought out by the photographs in plate 3. This fact becomes more interesting because no such differences were found in the plants from the soil extracts in group III. The extract saturated with $CaCO_3$ produced only 3 gm. of dry weight more than the untreated extract, as is shown in table 6. It is, therefore, reasonable to assume that the soil plants were much more benefited by the presence of $CaCO_3$ than were the solution plants. This assumption is further strengthened by two

TABLE 8

Composition and dry weight of plants from group IV grown on limed and unlimed soil

TANK NUMBER	TREATMENT	SOIL pH	TOPS	TOTAL	Ca	AVERAGE	Mg	AVERAGE	TOTAL N	AVERAGE	PROTEIN N	AVERAGE
			gm.		*per cent*		*per cent*		*per cent*		*per cent*	
13	Minerals	4.92	33.30		1.59		0.40		3.31		2.32	
				62.55		1.53		0.43		3.30		2.36
14	Minerals	4.92	29.25		1.47		0.46		3.29		2.40	
15	Minerals and $CaCO_3$	6.70	48.80		2.71		0.34		3.59		2.40	
				96.40		2.60		0.35		3.53		2.33
16	Minerals and $CaCO_3$	6.70	47.60		2.49		0.35		3.47		2.26	

facts: First, that the plants from the limed tanks absorbed a considerably higher percentage of calcium than did those from the "limed" solutions, and secondly that they contained 70 per cent more of this element than did the unlimed plants, as may be seen from table 8.

It may also be of interest to note that the magnesium content in the soil plants was lower than in those from any one of the culture solutions and that the higher Ca content was accompanied by a slightly lower magnesium content. The average magnesium content of the unlimed plants was 0.43 per cent whereas that of limed plants was 0.35 per cent. The amounts of nitrogen and of protein found in these plants did not show any pronounced differences from those found in the plants grown in the solutions. Comparing, however, the total nitrogen of the plants from the limed and unlimed soils, respectively, an increase of 0.23 per cent is observed with the application of $CaCO_3$. On the other hand, the average protein-nitrogen content of the plants from the two respective soils remained practically the same.

In general, the soil plants and the solution plants did not show any striking differences in composition. The application of $CaCO_3$, irrespective of the medium employed, produced similar effects on the growth of the plants. In each case where this salt was used there occurred a marked increase in the calcium, a considerable increase in the nitrogen, and no appreciable change in the protein nitrogen content of the plants. But so far as the total yield was concerned, the influence of $CaCO_3$ was strongly marked in the soil plants and little in the solution plants.

Finally, attention must be called to the fact that the total yield from series B was lower than that from series A. Since this phenomenon took place in all the culture solutions, it may be ascribed to the difference in the season. During the summer months when series B was carried out, the plants matured nearly two weeks earlier and did not make such a vigorous growth as did the plants from series A grown during the spring months.

DISCUSSION

A general survey of the average results obtained from the four groups of cultures brings out several interesting correlations. The average percentage values of the calcium content of the plants grown in culture solutions, in soil extract, or in soil, always follow the order of concentrations of this element in the medium, regardless of the calcium salt used and independently of the amount of nitrogen present. It appears, however, that the plants absorbed calcium more readily from $CaCO_3$ than from equivalent concentrations of this element in the form of $Ca(NO_3)_2$ or $CaCl_2$. The plants showed no tendency to absorb more calcium from $Ca(NO_3)_2$ than from $CaCl_2$ when present in the medium in equivalent concentrations of calcium, as was observed by Reed and Haas (43) in the case of citrus seedling.

On the other hand, the nitrogen content of the substratum appears to have no definite relation whatever to the nitrogen content of the plants, provided this element is present in the medium in sufficient concentration to supply the needs of the plants. Neither was the nitrogen content in the plants influenced by the concentration of calcium in the medium present in the form of $Ca(NO_3)_2$ or $CaCl_2$. In the presence of $CaCO_3$, however, the plants showed an appreciably higher total nitrogen content than in the presence of equivalent concentrations of calcium in the form of nitrate or chloride in the medium, irrespective of type; but in each instance this increased total nitrogen content of the plants was accompanied by a relatively much lower H-ion concentration of the medium than that of those in which the plants show no appreciable change in total nitrogen content with considerable variation in the calcium concentration of the media. This suggests that any superiority in the total nitrogen content of the plants over that of the checks is determined by the reaction and not by the calcium content of the solution, since higher increments of Ca in the medium had no influence upon the total nitrogen content of the plants unless accompanied by a corresponding decrease in the H-ion concentration.

The results do not offer a single example which might indicate a definite calcium-protein relationship in the soybean plants. In general the protein-nitrogen percentages ran considerably lower in all plants (except those grown in the soil in which nitrogen was deficient) than did the total nitrogen percentages, fluctuating between 2.25 per cent and 2.38 per cent. The protein content remained approximately constant and was independent of either the calcium or the total nitrogen content in the plants or in the media, except where the nitrogen supply in the media was insufficient for the requirements of the plants, as in the case of the soil extracts. These results lead to the assumption that the excess of nitrogen observed in the soybean plants grown on limed soil over that of the plants grown on unlimed soil is present only in the nonprotein form.

Thus the results secured from the present experiments emphasize strongly the fact that no direct relationship exists between the calcium and protein metabolism in the soybean plants. On the other hand it appears that higher quantities of total nitrogen were absorbed by the plants when grown in solutions containing $CaCO_3$ than in solutions where this salt was absent. It appears further, that both the calcium and nitrogen content of the plants increased when the pH of the solution was brought up to 6.0 or slightly higher by the addition of calcium carbonate.

SUMMARY AND CONCLUSIONS

Soybean plants grown to maturity on limed and unlimed soil, in soil extracts saturated with calcium carbonate, and in complete culture solutions containing varying concentrations of calcium and nitrogen, were analyzed for protein nitrogen, total nitrogen, calcium, and magnesium. Calcium chloride, calcium carbonate, and calcium nitrate were used in order to obtain different calcium-nitrogen ratios without otherwise disturbing the nutrient balance of the culture solutions.

1. A definite correlation between the amount of calcium in the culture solution and the calcium content of the plant was observed. The percentage of calcium in the plants increased with the increase in the concentration of this element in the culture solutions.

2. No definite correlation was observed between the amounts of nitrogen in the medium and in the plants. Increasing the nitrogen concentration of the culture solution did not appreciably alter the nitrogen content in the crop. Neither was the nitrogen content of the plants influenced by the calcium when calcium chloride or calcium nitrate was used; but a higher content of both nitrogen and calcium occurred in the plants in the presence of calcium carbonate than in the presence of either calcium nitrate or calcium chloride, irrespective of the medium employed.

3. High total nitrogen in the plants was definitely correlated with low H-ion concentrations in the medium.

4. No relationship was found between the calcium and the protein content in the soybean plants.

5. The plants showed higher rates of nitrogen absorption in the presence of $CaCO_3$ than in the presence of the other Ca compounds employed, but the increased rates of nitrogen absorption did not at all influence the protein content of the plants.

6. Culture solutions containing high concentrations of either calcium nitrate or calcium chloride produced plants which required less iron than did the plants grown in the solutions containing calcium carbonate.

7. In general, the soil plants did not show any striking differences in their composition from the plants grown in culture solutions. $CaCO_3$ had little or no accelerating influence upon the growth of the plants in the solution cultures, but had a marked accelerating effect upon the growth of the plants in the soil cultures.

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PLATE 1

GROUP I. PLANTS FROM SERIES B GROWN IN CULTURE SOLUTIONS (1, 2, 3, 4, 5) CONTAINING VARYING CONCENTRATIONS OF CALCIUM NITRATE

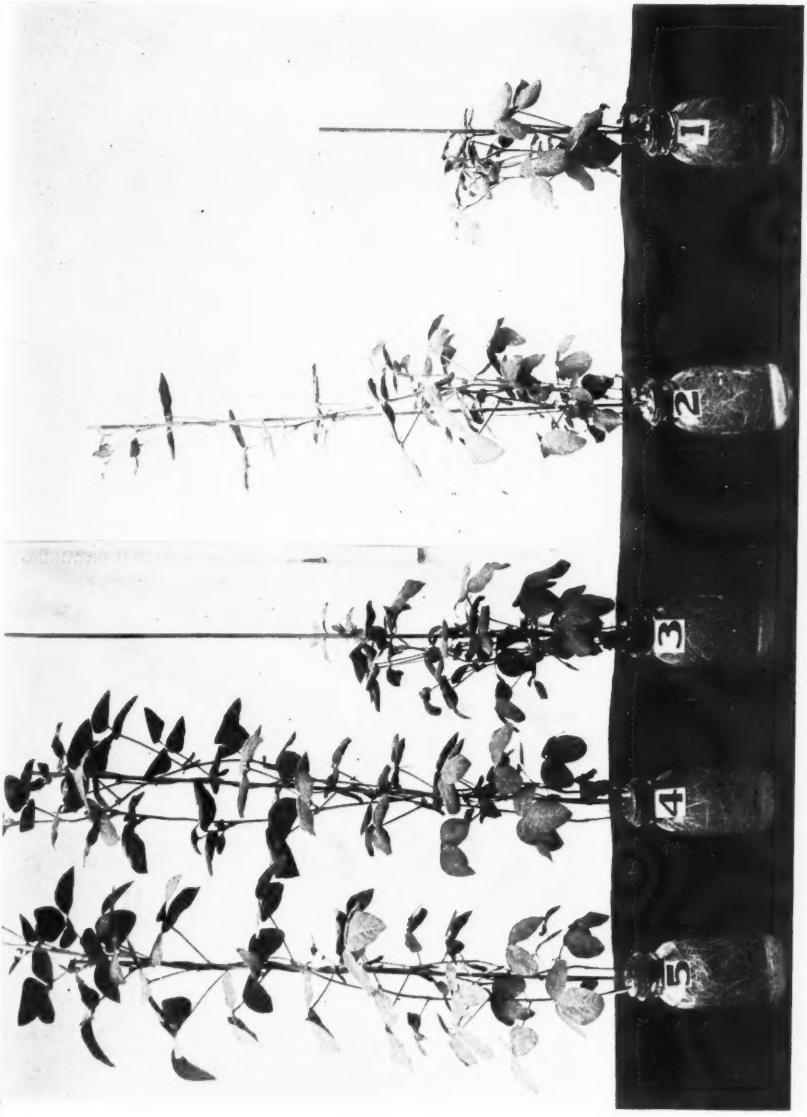

1
2
3
4
5

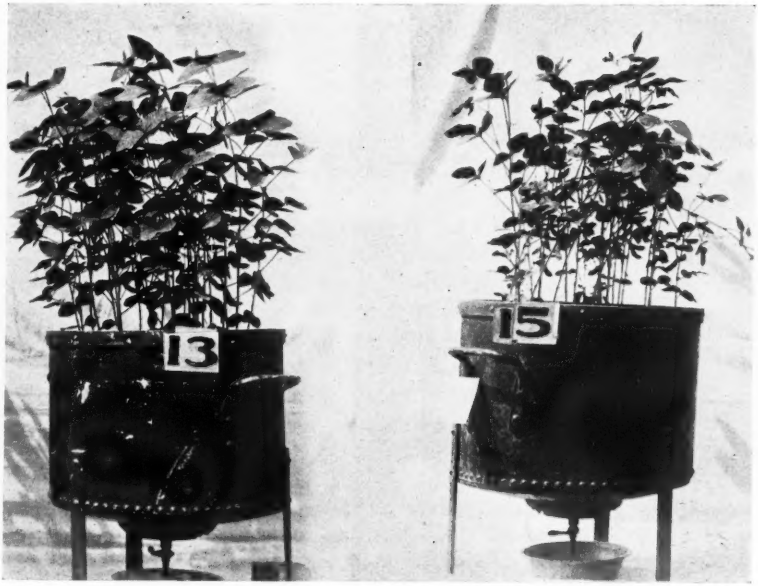
PLATE 2

GROUP II. PLANTS FROM SERIES B GROWN IN CULTURE SOLUTIONS (6, 7, 8) CONTAINING VARYING CONCENTRATIONS OF CALCIUM CHLORIDE

8
7
6

PLATE 3

GROUP IV. PLANTS GROWN IN LIMED (TANK 15) AND UNLIMED (TANK 13) SOILS


13
15

SOME OBSERVATIONS UPON THE EFFECT OF THE SIZE OF THE CONTAINER UPON THE CAPILLARY RISE OF WATER THROUGH SOIL COLUMNS[1]

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Although numerous records of the capillary rise of water through soil masses are to be found in agricultural literature, there is little reference made to the cross-sectional area of the soil column under consideration. It is clear that most workers in this field have assumed that the size of the column is a factor of little or no importance. Keen (3) gives a mathematical formula for the ultimate capillary rise of water through soil masses in which the average size of soil particles is known, but no factor in his formula indicates the effect of varying sizes of columns which might be put under observation. Hilgard (2) and other writers give the maximum capillary rise obtained in soils of varying properties, without mentioning the cross-sectional area of the columns used. Rotmistrov (6) working in the Odessa Experimental Field reports that a greater rise of water by capillarity was noted in small columns than in large columns when each size was filled with soil of similar texture. Risler and Wery (5) state that capillary rise is more rapid when large tubes are used for experimental observations than when small tubes are used, but no experimental evidence is offered to support the statement. No reference is made to the total rise experienced under these conditions.

The increasing use of tanks as a means of studying the use of water by plants and in observations upon the effect of a high water table upon plant growth prompted a careful study of the effect of the size of the container upon the capillary rise of water through soils.

PRELIMINARY OBSERVATIONS

Preliminary observations with the assistance of R. E. Storie[2] were made upon four cylindrical columns of sheet celluloid with exterior reinforcement of quarter-inch wire screen. These columns were filled with screened, well mixed, air-dried soil, uniformly packed and equal in volume weight. These columns were erected in a large constant temperature chamber, which was equipped with an electric heating element and a thermostat and maintained

[1] Published with the permission of the Director of the Experiment Station.

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at 85°F. A thermograph placed in the constant temperature chamber showed a maximum variation of 1.5°F. during the period of observation.

The columns were erected over a galvanized iron base pan in which the predetermined water level was maintained by a simple water stage regulator. The columns were submerged to a depth of 2 inches. Observations upon capillary rise through these several columns were made daily until the slowness of rate made less frequent observations acceptable. In all cases the magnitude of capillary rise as shown in table 1 measures the distance in centimeters from the constant water level to the point of capillary rise after the time interval noted. Table 1 gives a summary of the results obtained together with details of column sizes and the initial volume weights.

TABLE 1

Details of preliminary observations upon capillary rise through columns of varying cross sections

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4
Mean inside diameter, *inches*	1	$1\frac{1}{16}$	$3\frac{3}{4}$	$5\frac{7}{8}$
Initial volume weight, *gm.*	1.41	1.39	1.48	1.39
Discrepancy of volume weight from mean, *per cent*	−0.07	−2.11	+4.22	−2.11

DAYS	OBSERVED RISE			
	cm.	*cm.*	*cm.*	*cm.*
1	53.3	54.9	54.3	62.0
5	61.1	64.8	64.8	69.6
10	64.0	69.4	70.8	73.5
20	67.0	73.1	75.0	81.0
41	73.4	86.7	89.5	101.2
63	78.4	92.7	96.4	107.9

DETAIL OF APPARATUS

Although these results may be considered as indicative of a tendency, they are insufficient as a basis for a general statement with regard to the effect of the size of the container upon the capillary rise of water through soil masses. A second and more comprehensive installation was designed in October, 1924, to furnish more evidence.

In the new installation cylindrical columns were abandoned because of the difficulty of finding a suitable material for use in the larger sizes. Sheet celluloid has an unfortunate property of buckling upon handling which makes it unsuitable for use in cylinders larger than six inches in diameter. Glass in large sizes was considered as economically impractical. Square wooden columns, somewhat similar to those used by McLaughlin (4), except that the galvanized iron lining was omitted, were finally decided upon. Redwood lumber was used exclusively in the construction of the boxes. The unsurfaced faces of the boards were set inside the boxes in all cases. Backs and sides

were milled to fit exactly. Prescribed dimensions were maintained within the limits of good mill practice. Backs and sides were rabbeted in place and fastened with screws. Channels were milled on the side boards to receive plates of 26-ounce window glass which was cut to fit. Suitable cleats held the glass in place. In every case the bottom of the soil chamber was 2 inches above the bottom of the column. Bottoms were formed of pieces of perforated galvanized iron supported on cleats screwed to the sides of the columns. Fine screen and muslin cloth placed over this perforated plate prevented the soil from sifting through but at the same time gave ready entrance to water. All columns were painted on the inside with light asphalt paint to minimize the absorption of water by the wood. All columns were 5 feet 2 inches long, providing a net length of soil column of 5 feet.

All columns were square in cross section. The following sizes were used: 1 inch, 2 inches, 3 inches, 4 inches, 5 inches, 6 inches, 8 inches, and 12 inches square. Each size group contained four individuals in order that differences in rise of capillary water might logically be attributed to the size of the column and not to some individuality of a single column. Columns were so numbered that the last digit indicated the number of the individual within the size group. The first digit or the first two indicated the size group. This numbering will be adhered to in the following discussion. The columns were installed vertically in four galvanized iron base pans prepared for the purpose. Gage glasses were fixed to each of the pans so that the water level might readily be observed. A fine line on the gage glasses indicated the proper depth for a 2-inch submergence of all the columns in the tank. Constant water level devices were arranged for each of the tanks so that the predetermined water level might be maintained with a minimum of attendance. Distilled water was used throughout the course of the observations.

One individual of each size group was established in a separate base pan for observations on the rate of water absorption. Water-tight partitions divided this base pan into separate compartments in which the columns were erected. Individual water stage regulators, provided with calibrated reservoirs were established on each of these small compartments. Losses by evaporation from the surface of the water were minimized by lids of light galvanized iron carefully fitted over the tops of the individual compartments. It was discovered after the start of the capillary rise that the constant water level devices were not sufficiently accurate for determining the amount of water used by the several columns. This was especially true of the smaller columns which were mounted in relatively large tanks.

THE SOIL USED

The soil used was from the farm of the Branch College of Agriculture at Davis, California and is classified as Yolo fine sandy loam. It is a recent alluvial soil derived from sedimentary rocks. This series is representative of large scattered areas in California. The soil was carefully screened through a

2-mm. mesh, the coarser material being rejected. After screening, the soil was shoveled six times on a concrete floor to insure thorough mixing. A composite of random samples of the screened and mixed soil mass showed the mechanical analysis according to the method of the Bureau of Soils, given in table 2.

TABLE 2

Mechanical analysis of soil used in capillary rise columns

Bureau of Soils Method

GRADE	MECHANICAL ANALYSIS	
	mm.	*per cent*
Fine gravel	2–1	0
Coarse sand	1–0.5	0
Medium sand	0.5 –0.25	0.622
Fine sand	0.25–0.10	23.152
Very fine sand	0.10–0.05	54.866
Silt	0.05–0.005	13.326
Clay	Less than 0.005	8.710

TABLE 3

Weights of soil mass in capillary columns

Pounds per cubic foot

INDIVIDUAL IN SIZE GROUP	SIZE GROUP IN INCHES							
	1	2	3	4	5	6	8	12
1	81.82	83.07	82.12	82.84	82.86	82.27	82.27	80.18
2	85.51	81.82	81.85	82.80	82.69	81.89	81.85	81.89
3	85.32	82.81	82.43	82.39	83.41	82.54	82.50	81.02
4	84.67	82.92	83.35	82.69	82.69	81.82	83.26	80.18
Average	84.33	82.65	82.44	82.68	82.91	82.13	82.47	80.82
Average apparent density in pounds per cubic foot	1.35	1.33	1.32	1.33	1.33	1.32	1.32	1.30

The moisture equivalent for the soil in question was determined in accordance with the method indicated by Veihmeyer, Israelsen and Conrad (7). Four determinations were made, the average moisture equivalent being 16.64 per cent.

FILLING THE SOIL COLUMNS

Every care was used to provide uniform densities of soil masses within the several columns during the operation of packing. After a number of trials, the following method of filling was devised. A section of 2-inch leader pipe,

5 feet long, was lowered into the column to be filled. The leader pipe was then filled with the mixed soil by means of a funnel and scoop. As the leader pipe was lifted from the bottom of the column, soil was discharged. The soil was uniformly distributed over the bottom of the column by moving the pipe. It was found that the collection of larger granules against the glass face of the column could be lessened by keeping the soil mass slightly higher against the glass face than near the back of the box. Where an accumulation of larger particles behind the glass persisted, a piece of heavy iron wire flattened at one end was inserted between the soil mass and the glass. By manipulation of this wire a uniform soil mass was created behind the glass. Figure 1 shows the procedure of filling the soil columns. The irregularities in color on the faces of the columns already packed, as shown in this figure, are due to shadows. A flash light was used in making the exposure.

The soil used in filling each column was carefully weighed on a triple beam balance weighing to one gram. An 8-inch column was filled first. During the operation of filling, light uniform hammer blows on the back and sides of the column aided in securing uniform density throughout the soil mass. When the column was filled, the average density of the soil mass within the column was obtained by dividing the weight of equivalent oven-dry soil used in filling the column by the volume occupied by the soil mass. Other columns were filled upon the basis obtained from the first one filled. From a consideration of the relative volumes to be occupied by the several columns, the amount of soil necessary to bring about the required density could be readily determined in each case. Some columns were packed several times before an acceptable density was obtained. An apparent specific gravity of 1.3 is about what is found by observations for volume weight on this soil type under field conditions.

Table 3 gives the results obtained in these efforts to secure uniform packing.

METHOD OF OBSERVATION

Base pans were filled to the predetermined level at as near the same moment as possible. Not more than seven minutes elapsed between the filling of the first pan and the completion of the operation.

Observations on the capillary rise in the several columns were made by noting the position of the line separating the dry soil from the wetted soil. Recorded observations measured in centimeters the position of this line above the plane of the water level. Fine nails driven in the cleats covering the glass furnished convenient datum points for measurement. During the early course of the observation the line of demarcation between dry soil and wetted soil was extremely distinct, making observations easy and accurate. Toward the end of the run a feathering out was noted which presumably decreased the accuracy of the reported observations. This condition was especially true with the smaller sizes which showed no real increase in capillary rise near the end of the period of observation. Irregularities in the line across the glassed faces of the larger columns made accurate observations difficult. In cases where consider-

able irregularity (never more than 5 cm.) in the line of demarcation occurred, a large celluloid triangle was used to obtain the point of average rise. Observations were made by the same individual insofar as was possible during the entire period of rise in order that personal error might be reduced and compensated.

Observations were made at the same hour each day. During the initial period of the rise, observations were made daily. As the rate of rise became slower the time interval between readings became longer. The apparatus was visited daily to provide necessary distilled water and to adjust the constant

TABLE 4

Average rise of capillary moisture as observed in columns of varying cross-sectional areas after time intervals as noted

(Each value is the average of measurements of four columns)

DAYS RUN	SIZES OF SQUARE COLUMNS AS MEASURED BY ONE DIMENSION IN INCHES							
	1	2	3	4	5	6	8	12
	cm.	*cm.*	*cm.*	*cm.*	*cm.*	*cm.*	*cm.*	*cm.*
1	53.3	53.8	57.3	59.1	59.0	59.1	58.3	58.6
5	70.8	74.3	78.9	82.3	81.9	82.8	82.6	83.6
10	75.8	81.2	87.1	92.1	90.7	92.7	91.9	93.6
20	78.3	86.5	95.0	100.3	99.7	102.2	101.1	103.6
40	81.0	92.8	105.1	110.7	110.2	112.1	111.7	114.7
61	83.3	97.9	112.4	116.7	117.3	118.8	118.7	121.5
82	84.8	105.7	118.8	121.6	123.2	124.4	124.4	127.3
102	85.6	111.8	123.4	125.1	127.4	129.0	128.7	131.3
122	85.6	114.9	126.8	128.1	130.8	132.1	131.9	134.5
138	85.6	116.5	129.4	129.7	133.4	134.8	134.4	137.0
151	85.6	117.5	130.9	130.9	134.5	136.0	135.8	138.4
178	85.6	118.2	133.4	133.2	137.7	138.9	138.8	141.6
192	85.6	118.2	134.4	134.1	138.8	140.7	139.7	142.9
222	85.6	118.2	136.1	136.1	141.6	142.4	142.6	146.1
263	85.6	118.2	136.3	136.7	141.8	143.6	143.3	147.2

water level devices. The period of capillary rise extended from November 13, 1924 to August 4, 1925, or 263 days.

Figure 2 shows detail of installation and capillary rise in four of the smaller columns after sixteen days. The columns are 1 inch, 2 inches, 3 inches, and 4 inches square, reading from left to right.

SUMMARY OF OBSERVATIONS

The summary in table 4 shows the results of the observations made on the 32 capillary columns on different dates during the course of the rise. Detail with regard to individual columns is omitted for the sake of compactness, and the averages for the four columns making up the size group are recorded.

It is evident that the size of the column is a more important factor in determining the rise through capillary soil columns when the columns are relatively small than when the columns are large. In the four smallest groups every period of observation indicated a greater rise in the slowest column in one group than the highest rise in the next smaller group. The consistency of increase of rise with increase in size is reduced in the larger sizes. In fact the average rise for the 8-inch column for the time intervals noted was, in most cases, slightly less than for the 6-inch columns. A careful scrutiny of the detailed results of these observations indicate that a maximum difference of 11 cm. was recorded among the individuals of the same size group after the same time interval. The maximum differences due to the individuality of the columns were noted in the columns smaller than 25 square inches in cross-sectional area.

DISTRIBUTION OF MOISTURE

The moisture content present at different distances from the water table in each column was determined at the end of the experiment. The glass fronts of the columns were removed and the columns were tipped back slightly so that the top was about 2 inches from vertical. This was imperative in order that the dry soil near the tops of the columns might not fall out during the operation of sampling. A cheese sampler cutting a core $\frac{5}{8}$ inch in diameter was used to obtain a section of soil from the front to the rear of each column at the various heights. As it was impossible to obtain samples closer to the water level than 3 inches because of the sides of the water reservoirs, the sampling was limited at the lower end of the columns to this height.

The samples were dried at 100°C. for 48 hours, cooled to original room temperature, and the moisture content calculated on the basis of the oven-dry weight. The results of these observations for moisture content seem to indicate that in columns larger than 9 square inches in cross-sectional area the same moisture content can be expected at points representing the same percentage of the total rise above the plane of the water table. In columns smaller than 9 square inches in cross-sectional area, slightly higher percentages of moisture were found at the same relative elevations. In general the differences between the moisture contents taken from points representing the same percentage of the total rise in all the columns under consideration were never more than 3 per cent. Results of these moisture determinations indicate that a slightly higher percentage of moisture is to be found in the soil mass a few inches above the plane of the free water table than immediately above it as was first reported by McLaughlin (4). In the smaller sizes, such as the 1-inch, 2-inch, and 3-inch columns, this zone of maximum moisture content was only from 3 to 6 inches above the plane of the water table. In the 12-inch columns the zone of maximum moisture content was found to be from 11 to 15 inches above the water table.

In view of the differences in total rise in individuals within the same size group, it is unsatisfactory to report the zone of maximum moisture content

for a given size group in terms of centimeters. Table 5 gives the location of the zone of maximum moisture content for each of the columns in terms of its percentage of the total rise. The average of the four columns is also given.

TABLE 5

Location of zones of greatest moisture content in capillary columns of varying cross-sectional areas

Distance of zone of maximum water content above the water table is given as a percentage of the total rise

INDIVIDUAL WITHIN SIZE GROUP	SIZES OF SQUARE COLUMNS AS MEASURED BY ONE DIMENSION IN INCHES							
	1	2	3	4	5	6	8	12
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	8.3	12.2	16.2	27.3	27.2	20.9	19.9	20.7
2	15.8	11.0	19.0	22.9	21.2	26.9	21.3	20.8
3	9.3	11.0	20.3	18.2	16.0	19.4	17.6	20.7
4	14.2	15.2	22.9	22.7	18.2	26.2	26.2	20.7
Average....	11.7	12.4	19.6	22.8	20.7	23.5	21.3	20.7

TABLE 6

Observations on the uniformity of distribution of moisture in samples taken from the same elevation above the constant water level, but at different points within the cross section—column 123

LOCATION NUMBER	ELEVATION OF SURFACE SAMPLED, IN FEET ABOVE WATER LEVEL			
	1	2	3	4
1	33.2*	29.3	23.4	17.3
2	33.9	29.0	23.6	17.3
3	33.2	28.7	23.6	18.6
4	34.3	29.0	23.5	18.6
5	34.0	29.2	23.3	17.2
6	32.7	29.0	23.7	18.4
7	32.1	28.6	23.8	18.3
8	33.5	28.3	23.1	17.9
9	33.7	29.6	23.5	17.5
10	33.5	29.2	23.3	18.5
11	33.0	28.9	24.0	18.7
12	34.7	28.2	23.5	18.5
13	34.7	28.9	23.3	18.3
14	32.4	28.7	24.2	18.4
15	32.5	30.3	23.6	18.6
16	33.9	30.2	24.1	17.8

* Moisture contents in per cent—dry basis.

Although the point at which the maximum moisture content occurred is not the same distance above the water table in the four columns of the same size, there is considerable evidence that when columns with cross-sectional areas

of from 1 square inch to 16 square inches are considered, the zone of maximum moisture content becomes higher as the columns become larger. Increasing the size of the container to areas greater than 16 square inches seems ineffective in creating a further rise in the zone of maximum moisture content.

OBSERVATION UPON UNIFORMITY OF MOISTURE CONTENT WITHIN THE SAME HORIZONTAL PLANE

Column 123 was intensively sampled to determine whether a uniform rate of rise has been experienced at all points within the same cross section in the column. It may be assumed that if the greater rise exhibited in the larger columns were due to the greater rate of rise in the thin layer of soil lying in immediate contact with the sides of the column, a higher moisture content would be found in samples taken from this layer than in samples coming from the center of the column but in the same horizontal plane. Conversely, retardance toward rise caused by the material of the container would be reflected in a lesser moisture content near the sides of the container than in the center of the column.

In table 6 the results of soil moisture samples from planes at varying distances from the water table are given. When the sampling reported previously had been continued from the top of the column to the point 4 feet above the water table, the soil remaining above this point was removed. The top of the column remaining was divided into 16 equal parts by lines drawn with a spatula. A sample of the soil from the center of each of these 16 subdivisions was then obtained by boring downward a distance of 3 inches with the cheese sampler. These samples then represented the moisture content in the column under consideration, for the zone which extended from 45 to 48 inches above the water table. The locations within the plane are designated as follows:

Back of column

4 – 3 – 2 – 1

5 – 6 – 7 – 8

12 – 11 – 10 – 9

13 – 14 – 15 – 16

Glass face of column

The moisture content was determined as previously described and is expressed as percent on the oven-dry basis.

The same procedure was followed in planes 3 feet, 2 feet, and 1 foot above the water table. The results of these observatons are given in table 6. The locations refer to the key given above.

A study of the moisture contents at various points found in these four planes

of column 123, does not indicate any significant differences of moisture content within the same plane. The greatest differences found in the 16 locations in the same plane were in the plane 1 foot above the water level. Samples for this determination were taken from a zone from 9 to 12 inches above the water level. In this plane the highest moisture contents were not found to be segregated in the center of the plane nor along the sides of the column. Reference to table 5 indicates that the maximum water content in column 123 was found at a point 20.7 per cent of the total distance from the water table to the elevation of maximum rise. Since the maximum rise in column 123 was almost 5 feet, it is evident that samples taken from a plane 1 foot above the water level come from the zone of maximum moisture content. This understanding may explain the erratic nature of the results from the 1-foot plane. It seems fair to conclude from the data presented that the moisture was fairly uniformly distributed within the various planes and that there was no consistent difference in moisture content between the samples taken from the center of the columns and those taken near the sides of the columns. There is some evidence also that the heights of rise as noted through the glassed fronts of the columns are a fair index of the moisture movement upward by capillarity.

No satisfactory explanation of the causes for the results listed above has occurred to the authors at this time. The evident suggestion that the cause is variation in temperatures on different parts of the column does not completely satisfy all the conditions, since in the preliminary observations when all the columns were maintained in a constant temperature chamber there were indications that the size of the container was significant in determining the capillary rise of water through soil columns. In the later installation every effort was made to eliminate wide variations in temperature between size groups in the bank of soil columns. Convenience of installation made it desirable that columns of the same size be scattered throughout the assembly instead of placing all the individuals of a size together. It seems doubtful if localized differences in temperature could effect such a consistent variation as is reported in rise among the sizes.

The suggestion that the lesser rise in the smaller columns is due to greater frictional resistance by the sides of the columns is perhaps logical. Careful scrutiny will show, however, that the degree of retardance in the smaller columns has no relation to the ratios of cross-sectional areas of columns to their perimeters. This suggestion is still further disputed by the uniformity of moisture content in the cross section of a column. Preliminary observations with cylindrical columns of celluloid showed results of the same nature as those later reported. It is probable that the material in which the soil columns are contained is of minor importance, and if so it is probable that the resistance to rise because of friction on the container may be disregarded.

Colloidal changes within the soil mass, due to the progressive wetting, are probably the controlling influences. Still the evidence given by Bouyoucos (1) shows that when soils are unequally moistened the swelling of certain types

of soil colloids tends to set up unequal stresses. In the case of the smaller columns these stresses would probably result in greater compactness than in the larger columns because of the greater perimeter per unit area of cross section. Increasing the compactness in a column would supposedly reduce the effective diameters of the capillary channels and result in a greater ultimate rise, but would reduce the rate. Such, however, was not found to be the case in the columns under consideration. The smaller columns not only rose more slowly than the larger columns but reached a maximum rise after one-third of the period of observation had elapsed.

It is hoped that this problem can be still further investigated in the near future.

SUMMARY

1. Evidence is furnished that the extent of capillary rise through soil masses from a free water table is affected by the cross-sectional area of the column under consideration.

2. In general large columns show a greater rise after a given time than small columns.

3. From the observations reported, size of the container is of greatest importance in columns with a cross-sectional area of less than twenty-five square inches.

4. Intensive soil moisture samples indicate that there is no uniform distribution of moisture throughout the length of the capillary columns. A point or zone of maximum moisture content is found at an appreciable distance above the water table.

5. There is some evidence that in columns of small cross-sectional areas the distance of this zone of maximum moisture content above the water level varies with the size of the column, this distance being greater as the columns become larger. When the cross-sectional areas of columns become greater than about sixteen square inches, further increases in size do not affect the relative position of this zone of maximum moisture content.

6. Moisture samples taken at various points in the same horizontal plane within the column indicate a fairly uniform and consistent moisture content at all points.

7. No experimental evidence is available to support the belief that the upward rise as indicated through the glassed face of a capillary column is not indicative of the rise within the whole soil mass.

REFERENCES

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(6) Rotmistrov, V. G. 1913 The nature of drought, Odessa experimental field.
(7) Veihmeyer, F. J., Israelson, O. E., Conrad, J. P. 1924 The moisture equivalent as influenced by the amount of soil used in its determination. Calif. Agr. Exp. Sta. Tech. Paper 16.

PLATE 1

Fig. 1. Detail of procedure used in filling capillary rise columns.

Fig. 2. Section of capillary column assembly used to demonstrate the effect of the size of the container upon capillary rise from a free water table. The photograph shows the extent of rise after 16 days.

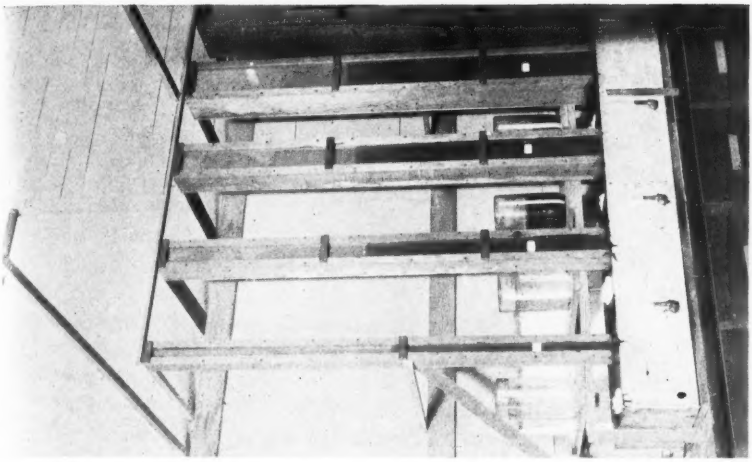

FIG. 2

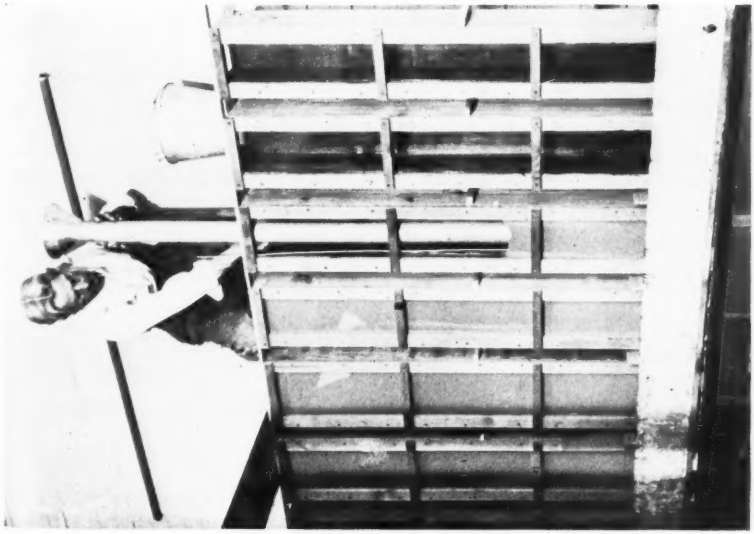

FIG. 1

UNIV. OF MICH.

REVIEW OF GERMAN LITERATURE ON SOIL SCIENCE AND PLANT PHYSIOLOGY IN 1925[1]

Received for publication February 18, 1926

SOIL SCIENCE

BALKS, R. *Investigations on the formation and decomposition of humus in the soil.* (Landw. Vers. Sta. 53: 221–258.)

The author investigated samples from six different soils which had been heated with stable manure. The formation and decomposition of humus in the soil were determined quantitatively at different times.

BLANCK, E., AND ALTEN, F. *Contributions to characterization and classification of "Roserde."* (Landw. Vers. Sta. 53: 41–72.)

The authors described the way in which "Roserde" had been classified up to the present. The following conclusion was drawn from their own investigation:

When for a sample of "Roserde" the hygroscopicity and the amounts of Al_2O_3 and Fe_2O_3 soluble in HCl were determined it was possible to state whether the soil should be classified as belonging to the Mediterranean or to the tropical type of "Roserde."

BLANCK, E., AND ALTEN, F. *Experimental contributions on the formation of "Roserde."* (Landw. Vers. Sta. 53: 73–90.)

The authors carried out leaching experiments and came to the following conclusion:

Magnesite is of little importance for the formation of "Roserde." Precipitation of iron may be prevented by the presence of colloidal humus substances even if lime is present at the same time.

BOBKO, E. W., AND DRUSCHININ, D. W. *Influence of certain factors upon the reaction of soil solution.* (Ztschr. Pflanzenernähr, u. Düngung. (A) 5: 45–369.)

The authors investigated the influence of different soil water ratios upon the soil solution. They compared the pH values of water extracts with those of soil solutions. Further, they discussed the influence of lime application upon soil reaction.

FRESENIUS, L. *The present state of the question of soil acidity.* (Ztschr. Pflanzenernähr. u. Düngung. (B) 4: 200–212.)

[1] These abstracts were prepared by Chr. Krull and E. A. Mitscherlich, University of Königsberg, Prussia, and translated from the German by S. T. Jensen, New Jersey Agricultural Experiment Stations.

The author reviews the different questions in the problems of soil acidity and the corresponding methods for its determination.

GEHRING, A., AND WEHRMANN, O. *Studies on the effect of lime upon soils.* (Landw. Vers. Sta. 53: 179–335.)

The authors studied in the laboratory the effect of "Endlauigekalk" and "Kalikalk" (industrial vasse products) upon the physical and biological conditions of the soil. Further they studied in the field the effect of various kinds of lime upon the crop yield and upon the CO_2 production of soils. Finally they determined the degree of saturation of different soils with lime according to Hissink's method. They reported their own method for determining the maximum combining power of a soil with lime.

GEHRING, A., AND SCHÜLKE, G. *On the effect on soils of some natural varieties of lime and marl and of some Ca and Mg compounds.* (Ztschr. Pflanzenernähr. u. Düngung. (B) 4: 113–139.)

The authors investigated the solubility of different varieties of lime of different degrees of coarseness. Further, the influence of CaO, $CaCO_3$, $CaSO_4$, MgO, $MgCO_3$, and $MgSO_4$ upon the physical, chemical, and biological processes in soils was studied.

HAGER, G. *On the determination of acidity in mineral soils.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 159–177.)

The author discussed the different forms of acidity. He concluded from his experiments, that Kappen's explanation of the exchange acidity is correct.

HISSINK, D. J. *The saturation condition of the soil: A. Mineral soils (clay soils.)* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 137–158.)

The author studied first the saturation condition of a number of clay soils as far as exchangeable bases were concerned, and then the question of liming.

HISSINK, D. J. *The method of mechanical soil analysis.* (Internatl. Soc. Soil Sci. Proc. 1:137–156.)

The author first discussed the preliminary treatment of soil samples with HCl, H_2O_2, and NH_4OH, before the sedimentation process in an Atterberg cylinder was carried out. Then he recommended a new method for preliminary treatment as worked out in his laboratory. Finally he discussed the sedimentation methods devised by Wiegner, Odeir, Robinson and Kraus.

KAPPEN, H., AND BELING, W. *On the quinhydrone method, the relation between its results and the different kinds of soil acidity.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 6: 1–26.)

The authors tested Biilmann's quinhydrone method for electrometric pH determinations. Then by means of this method they studied the exchange

acidity and the hydrolytic acidity of a large number of soils. A number of very interesting results, from the point of view of the method, were obtained.

KAPPEN, H., AND BOLLENBECK, K. *On the importance of the different kinds of soil acidity for making little-soluble phosphates more soluble.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 1–29.)

The authors used the following acid substances in their experiments: Humic acid from sugar obtained by Berthelot's and Andre's method, natural humic acid, amorphous SiO_2, permutite and field soil possessing exchange acidity. The dissolving effects of the three kinds of acidity upon phosphates were studied in those substances. The phosphates used in the experiments were tricalcium phosphate and natural phosphorites.

KNICKMANN, E. *Investigations on the question of soil acidity.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 5: 1–92.)

Having discussed the present state of the soil acidity problem, the author studied the appearance of the different forms of acidity in profiles from clay, sand, and humus soils. The methods of determinations were critically discussed. The development of the effect of lime upon exchange acidity and hydrolytic acidity was studied experimentally.

KNICKMANN, E., AND HELBIG, M. *Investigations on soil exhaustion.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 5: 209–248).

The authors studied the physical and chemical properties of exhausted forest soil and of poor humus. In this connection investigations on soil acidity were made.

NICKLAS, H., AND HOCK, A. *On the question of exchange acidity in soils and the relation between titration acidity and actual acidity.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 5: 370–392.)

The authors studied the behavior of the exchange acidity for pure solutions of Al salts and for a number of different kinds of soils. The corresponding relations between titration acidity and actual acidity were also studied.

RENNER, W. *The influence of various fertilizers including lime and phosphates upon the structure of the soil.* (Ztschr. Pflanzenernähr. u. Düngung. (B) 4: 417–451).

The author studied the effect of CaO, $CaCO_3$, $CaSO_4$, superphosphate, Thomas phosphate, and Renania phosphate upon the structure of different soils. He concluded from his experiments that $CaSO_4$ and super phosphate seemed to have an unfavorable effect upon soil structure as opposed to that of the other fertilizers.

SCHEFFER, F. *On the nature and causes of the transformation of burned lime in the soil.* (Jour. Landw. 72: 201–235.)

The author summarized his experimental results as follows:

1. In soils with a small lime content the transformation of CaO into $CaCO_3$, as far as studied, does not take place quantitatively even with neutral reaction. A large amount of CaO is taken up in another way.

2. The experimental results of E. Blanck and G. Hager were completely substantiated.

3. Probably a complete transformation of CaO into $CaCO_3$ takes place only in soils containing an appreciable amount of $CaCO_3$.

4. Completion of the quantitative transformation is prevented by the presence of absorbing substances in the soil.

5. It was possible to demonstrate that silica gel and the mixture gel SiO_2-Al_2O_3 were absorbing substances.

6. SiO_2 gel is capable of decomposing $CaCO_3$.

PLANT PHYSIOLOGY

ARND, TH. *The humic acids, their influence upon the life of micro-organisms in peat soils and the methods of acidity determination.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 53–72.)

By determining ammonia formation, nitrification, and denitrification, the author studied the influence of humic acids upon the life of microörganisms in different kinds of peat. The peat samples used were moor peat, heath peat, and low peat bog.

ARRHENIUS, O. *The lime requirement of soils from a plant physiological viewpoint: II. Soil reaction and the growth of higher plants.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 30–52.)

The author continued his review on this subject published earlier in *Zeitschrift für Pflanzenernährung und Düngung.* He called attention to the fact that different plant varieties are different in their behavior to soil reaction. The paper contains an extensive review of the literature.

ARRHENIUS, O. *The lime requirement of soil: III. The influence of soil reaction upon biological physico-chemical soil factors.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 348–358.)

Using his own experiments and those of other investigators, the author demonstrated the great importance of liming and of soil reaction for all factors of soils.

ARRHENIUS, O. *The lime requirement of soil: IV. Practical applications of the study of soil reaction.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 5: 195–199).

The acid and alkaline conditions of soils from certain estates were presented graphically on a colored map. It was thus demonstrated how the study of soil acidity could be used for practical purposes.

DENSCH AND HUNNIUS. *Studies on the growth of oats. The water content of the soil at different times during the period of growth and its influence on crop*

yield. The ratio between grains and straw and the assimilation of plant nutrients, especially phosphoric acid. (Landw. Vers. Sta. 53: 91–102.)

Assimilation of phosphoric acid, of potassium, and of nitrogen could be observed, even at the end of the period of growth, when water supply was abundant. In dry periods assimilation, especially that of nitrogen, was much decreased.

KAPPEN, H., AND LUKACS, M. *On the physiological reaction of chemical fertilizers.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4. 249–270.)

The authors grew cultures of corn, mustard, and buckwheat in sand cultures and in culture solutions. They studied the effect of the different plants upon the reaction of the medium in which they were grown.

KIRSTE, H. *On the growth of plants in acid soils.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 5: 129–194.)

The author studied the conditions of soil acidity and its influence upon plant growth. Extensive field and pot experiments were carried out with different cultivated plants. Various kinds of fertilizers and increasing amounts of lime were applied.

KRULL, CHR. *Remarks on Reinau's invesigations on carbonic acid.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 359–367.)

The author discussed and criticized Reiman's work of 1924 on the CO_2 question.

LEMMERMANN, O., AND WIESSMANN, H. *Studies on the increases in crop yield due to silica.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 4: 265–315.)

When plants are grown without a sufficient supply of phosphoric acid, an addition of silica will increase the crops. The authors explain this fact by the dissolving effect of silica upon phosphates.

MEVIUS, W. *The direct influence of H-ion concentration in culture mediums upon plant cells.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 6: 89–98.)

The author studied the hydrogen-ion concentration and its constancy in the cell sap, and the relation between the pH values in the plant cells and in the culture solutions. He concluded from his experiments that the effect of H-ion concentration in a culture solution is controlled by the permeability of the cell.

MITSCHERLICH, E. A. *The strain and variety experiment and its influence on the methods of plant breeding.* (Mitt. Deut. Landw. Gesell. 50.)

The author discussed the methods used hitherto in field experiments with different strains and varieties of plants. He claimed the necessity of following new lines in plant breeding, for instance: I. Breed plants which require

certain amounts of water at definite times during the growth period. II. Breed plants resistant to acid or alkaline soil reaction. The author tested the effect of reaction upon two different strains of oats and barley, and demonstrated that pot experiments are well suited for such tests.

MITSCHERLICH. E. A. *Plant physiological investigations on soil acidity.* (Landw. Vers. Sta. 54: 36–42.)

Fifty soil samples were investigated. From the results the author concluded that no correlation exists between the actual acidity and the buffering power of soils. He emphasized that only by vegetation experiments would it be possible to obtain a clear picture of the reaction conditions in the soil.

MITSCHERLICH, E. A. *A contribution to the question of CO_2 as fertilizer.* (Angew. Bot. 7: 24–40.)

The author argued against Reinau's work (1924), mentioned above, on the CO_2 question. He discusses his own standpoint in regard to that problem and the work of Janert, Spirgatis and Lamberg on light and CO_2 as factors of growth.

MITSCHERLICH, E. A. *On the method of determining fertilizer requirements of the soil: II. By the Mitscherlich method.* (Ztschr. Pflanzenernähr. u. Düngung. (B) 4: 193–199, 473–478.)

In two articles (*Zeitschrift für Pflanzenernährung und Düngung.* (B) 4: 25–31, 273–285.) Gerlach criticized the plant physiological method devised by the author for the determination of plant nutrients in the soil. The author argued against this criticism.

PRIANISCHNIKOV, D. N. *On the physiological character of ammonium nitrate.* (Ztschr. Pflanzenernähr. Düngung. (A) 4: 242–250.)

The author carried out experiments with sand cultures and with nutrient solutions. He concluded from his experiments, that the physiological acidity of ammonium nitrate was more predominant than its amphoteric properties.

REINAU, E. *Carbonic acid from soils and from the atmosphere as factors in agriculture.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 5: 393–395.)

The author argued against Krull's criticism[2] of Reinau's CO_2 theories.

SMITH, W. *Carbonic acid as a stimulant and as building material.* (Ztschr. Pflanzenernähr. u. Düngung. (B) 4: 162–171.)

The author discussed the investigations of Lundegardh and demonstrated by his experiments the effect of CO_2 as a stimulant.

[2] See KRULL, CHR. *Remarks on Reinan's investigations on carbonic acid*, p. 7 of this paper.

USCHIDRAWEITS, H. *Stimulation experiments.* Dissertation, Königsberg, Prussia. (Bot. Arch. 1925: 119–133.)

The author carried out stimulation experiments for a series of plants. The materials used were $MgSO_4$ and $MnSO_4$. The increase in crop yield reported by Popoff was not obtained.

WAGNER, H. *The relation of plant growth to physical chemistry.* (Landw. Jahrb. 62: 785–808.)

The author carried out vegetation experiments with oats. The plants were grown in pot cultures and the soil was kept at its maximum water-holding capacity. The course of growth was studied when different amounts of water were available. With Mitscherlich's law as a basis, the relation of plant growth to physical chemistry was discussed.

WALTER, H. *The saturation of plants with water, and its importance for plant growth.* (Ztschr. Pflanzenernähr. u. Düngung. (A) 6: 65–88.)

The author discussed investigations on the swelling of the protoplasm of lower plant organisms. He demonstrated that the life processes of higher plants depends in a similar way upon the degree of water saturation of cells. The same, of course, holds true for the crop yield of our cultivated plants.

WEISS, F. *The action factor when the action law of the growth factors is applied to the drill distance of cultivated plants.* Dissertation, Königsberg, Prussia. (Bot. Arch. 1925: 377–385.)

The author applied Mitscherlich's action law of the growth factors to the drill distance between plants. The relation of the action factor to different kinds of cultivated plants was studied.

ON THE ORIGIN AND NATURE OF SOIL ORGANIC MATTER OR SOIL "HUMUS": II. METHOD OF DETERMINING HUMUS IN THE SOIL[1]

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The methods commonly employed for measuring quantitatively the soil organic matter or soil "humus" are based upon:

1. The determination of total carbon in the soil; the quantity thus obtained is multiplied by 1.74 to give the soil organic matter; 2. the treatment of the soil with an oxidizing agent, such as dilute H_2O_2, permanganate, or silver chromate; the quantity thus obtained is presumably the more available part of the soil organic matter; 3. the treatment of the soil with a dilute alkali solution; this method presumably allows differentiation between natural organic matter added to the soil and the soil organic matter or "humus."

The last method has come into general use, especially in connection with the study of the nature of the soil organic matter. However, by varying the kind of alkali used for the extraction of the soil organic matter, or the concentration of the alkali, and the length of its action upon the soil as well as the preliminary treatment of the soil with other reagents, investigators obtained varying results. As a result of this, the determination of total carbon in the soil, either by dry combustion or by wet combustion (by means of chromic and sulfuric acids), is frequently used for measuring the soil organic matter. This method is suitable for measuring the total organic matter of the soil, but in a study of the origin and nature of this organic matter, a method had to be used whereby one could differentiate between different constituents of organic materials and especially between the natural organic matter and the soil organic matter. The use of alkalies for the extraction of the latter also offered a means of separating it into several fractions. Whenever methods were available for determining quantitatively definite chemical elements of compounds, they have been utilized.

The soil organic matter, whether from mineral or peat soils has been commonly divided, on the basis of solubility in alkali solutions, into several fractions. The relative amounts of the different fractions depend largely upon the nature of the alkali and its concentration. Since different reagents have been used by different investigators, there is no basis whatsoever for comparison between the results thus obtained. When sodium hydroxide is used for

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extracting the soil "humus" and the solution thus obtained is neutralized with hydrochloric acid, a precipitate is formed. When an excess of acid is added over that necessary for the neutralization of the alkali, a part of the precipitate goes again into solution. When the precipitate is washed with sufficient acid, an organic preparation practically free from inorganic matter is obtained. This preparation has been usually referred to as "humic acid" and has frequently been further subdivided, on the basis of solubility in alcohol or pyridine. However, since no definite proof has been submitted that these substances are definite chemical complexes and as the available information seems to point to the fact that they consist of more than one constituent, it may be convenient to term the part of the soil organic matter soluble in alkalies and precipitated by acids as the α-fraction of the "soil organic matter." When the acid solution, obtained after the α-fraction has been removed, is neutralized with an alkali, another precipitate is formed which is soluble both in alkalies and in acids and which can be termed conveniently the β-fraction of the soil organic matter. This fraction is usually absent in peat soils and is found abundantly in mineral soils; it contains about 30 per cent organic and about 70 per cent inorganic materials, largely aluminum, as shown by the carbon, nitrogen, and ash content.

The use of the colorimeter for comparing the alkaline extract of soils may perhaps be satisfactory for measuring the "humic acid" content of peat soils, where the α-fraction is predominant, but it cannot be applied to ordinary mineral soils, which contain different proportions of the α- and β-fractions, the latter being only light brown in color and not black as the α-fraction is.

Soil organic matter can be thus divided into 4 distinct groups of substances, some of which possess well defined chemical characteristics:

1. Those substances which are insoluble in dilute alkaline solutions even after prolonged extraction, either in the cold or at 100°C. Here belong various constituents of natural organic matter, which have not yet been decomposed or which are still in the process of decomposition, and certain substances of microbial origin, such as chitin and various mycohexosans. This fraction of soil organic matter contains the so-called "humus coal" or substances of a high carbon and a low oxygen and nitrogen content and has been referred to in the older literature as "humin" or "ulmin."

2. That part of the soil organic matter which is soluble in dilute alkali solutions (1.5 to 5.0 per cent NaOH), after a shorter or longer period of extraction in the cold or under pressure, and which is precipitated by an excess of hydrochloric acid. This group comprises the so-called "humic acids" (α-fraction) and is characterized by a definite nitrogen content, usually ranging from 2.0 to 4.0 per cent, with an average of 3.0 to 3.5 per cent, and by a low ash content (about 1 per cent); certain "humic acids" from fresh peat and fresh forest mold may contain a much lower amount of nitrogen for the same amount of carbon. This group received the attention of the great majority of investigators of soil organic matter, as has been pointed out. Some claimed (1) that it is a colloidal substance very complex in composition; others (3,6) tried to prove that it is a pure chemical substance of a comparatively simple structure and of a low molecular weight. The recent theories seem to indicate that it may be largely lignin in nature, although its nitrogen content has not yet been accounted for.

3. Those substances which are soluble in alkalies (1.5 to 5.0 per cent NaOH) and in hydrochloric acid, but are precipitated at a definite isoelectric zone (pH 4.6 to 5.0). This is

an organic-inorganic complex (β-fraction) and is characteristic of mineral soils. Its presence was recorded in the soil by some investigators (7, 4) but no reference is found in the literature concerning its abundance in the soil, its relation to the α-fraction ("humic acids"), or its rôle in the soil. The ash content of this preparation consists almost entirely of aluminum. The total carbon content of the preparation is about 15 per cent and the total nitrogen 1 per cent, giving a carbon:nitrogen ratio similar to that of the α-fraction. The substance is probably an aluminum-organic compound ("Al-humate"). It is of interest to note here that by the use of ammonium hydroxide, no β-fraction is obtained, although Blanck and Alten (2) have shown that the treatment of soil with NH_4OH results in considerable losses, largely Al_2O_3. The nature of the α and β fractions of the soil organic matter will be discussed in detail later.

4. Those substances which are made water-soluble as a result of the alkali treatment—the so-called "crenic" and "apocrenic" acids or "fulvic" acid.

The last three groups of substances comprise the so-called soil "humus" and may amount, if the extraction with alkali is continued long enough, to 60 to 85 per cent of the total soil organic matter, as measured both by the carbon and nitrogen content. The terms soil "humus" and alkaline extract of soil have become almost synonymous, although some investigators still speak of "humus" as the total soil organic matter. The process of "humification" is usually spoken of as the transformation of natural organic matter into the more resistant soil organic matter or the organic matter soluble in alkalies.

The fact that natural materials contain only 15 to 30 per cent of substances soluble in alkalies and not soluble in water (except some hemicelluloses), while the soil organic matter contains 60 to 80 per cent of such materials, would seem to point to a distinct difference in the nature of the substances and to certain specific processes which bring about the change from the natural organic matter into the soil organic matter.

The solubility of a large part of the soil organic matter in alkalies offers a good starting point for the investigation of its nature. Even if not all the soil organic matter is soluble and even if different soils vary in the amount that becomes soluble, it is still the best, if not the only, general method which differentiates definitely between the larger part of the plant residues, for example, and the so-called soil "humus."

After it has been decided, however, to use the solubility of the soil organic matter in alkalies as an index of the "humus" content in the soil, or of the amount of dark colored organic matter which has become an integral part of the soil and which does not decompose at all or with great difficulty, it still remains to determine how to use this method so as to obtain always comparable quantitative results. A survey of the literature, presented previously, shows that there is a total lack of agreement as to the comparative value of the different methods for the determination of "humus" in the soil. Many students of soils, including soil chemists, seem to have become so much discouraged with the unsatisfactory results obtained from these determinations that they have given up altogether the determination of "humus" in the soil and have limited

themselves to the determination of total carbon. Witness the fact that, after prolonged discussions on the subject, the method of "humus" determination has been excluded entirely from the more recent editions of the "Official Methods of the Agricultural Chemists."

This lack of agreement concerning the method of determination of a substance or a group of substances which lie at the very basis of soil fertility and soil science in general, is due largely to the lack of sufficient knowledge as to just what is being determined. As a result, there was no criterion for determining the efficiency of the various methods. The lack of comparable methods served further to becloud our conception of the nature of the soil organic matter. Certainly the various names and formulae did not serve to advance our understanding of this subject.

The method to be decided upon in the following pages would, of course, be only arbitrary, until some more definite information is obtained concerning the origin and nature of the soil "humus." In the following studies on the origin of this substance or group of substances in the soil, however, as some method had to be employed for measuring quantitatively the formation, accumulation, and decomposition of this "humus" in the soil, the method which would allow the determination of the largest amount of this material, even if only an arbitrary part of it, had to be selected.

EXPERIMENTAL

The following studies were outlined with the idea of determining the nature of the alkali to be used for extracting the soil "humus;" its concentration, and the length and nature of its action which would give the largest yield of "humus" from different soils. Of the various ingredient elements of this organic matter, nitrogen and carbon were most important in this study. The ash content and its nature were left out of consideration for the present.

"Humus" is commonly believed to exist in the soil in a form combined with bases, as humate. Preliminary treatment of the soil with hydrochloric acid is supposed to break up the humates, liberating the free "humic acid," which is then extracted by the alkali treatment. The first three experiments reported here deal with the influence of the preliminary treatment of soil with 1 or 2 per cent HCl upon the amount of "humus" extracted by alkalies. The acid treatment was continued for 2 hours, followed by washing with distilled water. Either 5 per cent NaOH or 4 per cent NH_4OH was then added (100-cc. portions to 100 gm. of soil) and allowed to act for 48 hours in the cold. The liquid was then filtered off and, in the case of the NaOH-treated soils, the whole liquid was precipitated with 10 per cent HCl; whereas in the case of the NH_4OH-treated soils, an aliquot portion of the liquid was evaporated to dryness on a water bath, weighed, ignited, and weighed again and the difference taken to represent the amount of "humus" in the soil. The results presented in tables 1 and 2 indicate quite definitely that the preliminary treatment of the soil with 1 or 2 per cent HCl not only does not increase the amount of "humus"

extracted, but tends to decrease it, especially in the case of certain soils and with the 2 per cent acid. The reduction is marked both in the α and β-fractions. The reason for this reduction can be readily understood when one considers the existence of the β-fraction in the soil, an organic-inorganic complex soluble both in NaOH and in HCl. The preliminary treatment of the soil with acid tends to remove this fraction from the soil and, therefore, also a part of the soil organic matter. In the case of forest and peat soils, preliminary treatment with HCl did not influence materially the amount of "humus"

TABLE 1

Influence of preliminary treatment of soil with HCl (1 per cent) upon the amount of "humus" extracted from a heavily manured (5A) and unmanured (7A) soil

100 gm. of soil extracted with 5 per cent NaOH

SOIL	EXTRACTION WITH HCl	α-FRACTION		β-FRACTION		NITROGEN IN SOLUTION AFTER β-FRACTION HAS BEEN REMOVED
		Yield	N content	Yield	N content	
		mgm.	*per cent*	*mgm.*	*per cent*	*mgm.*
5A	+	667		1,236	1.03	28.4
5A	−	805	2.97	1,371	1.35	27.8
7A	+	333		1,226	1.05	9.8
7A	−	353	2.55	1,493	0.87	14.4

TABLE 2

Influence of ether and acid (2 per cent HCl) upon the amount of "humus" extracted by two portions of 2.5 per cent NaOH from a Sassafras soil

EXTRACTION	α-FRACTION		β-FRACTION		NITROGEN CONTENT OF SOLUTION FROM β	HCl EXTRACT PRECIPITATED WITH NaOH YIELD
	Yield	N content	Yield	N content		
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
None	851	23.6	926	14.8	14.0	
Ether	904	25.5	953	16.4	11.7	
HCl	406	15.1	572	17.5	7.8	1,716
Ether + HCl	423	15.3	584	19.6	9.3	1,847

extracted by alkalies, because these soils contain none or only traces of the β-fraction.

A comparison of NaOH and NH_4OH (table 3) as reagents for the extraction of soil "humus" shows that NH_4OH extracts a smaller amount of "humus" than NaOH; the α-fraction alone extracted by the NaOH is almost equivalent to the total amount extracted by the NH_4OH. The β-fraction consists of about 30 per cent of organic matter and is extracted only by the NaOH. Filtration of the NH_4OH extract is much more difficult than that of the NaOH extract. The presence of nitrogen in the reagent prevents an accurate analysis of the

nitrogen content of the extracted organic matter. This makes preferable the use of NaOH for the extraction of soil "humus."

As to the influence of concentration of alkali upon the amount of "humus" extracted, the results in table 4 indicate that the use of 2.5 per cent NaOH (100 cc. of reagent for 100 gm. of soil), extracting at 15 pounds pressure for 30 minutes, filtering through paper, then extracting the residual soil with a fresh quantity of 100 cc. of 2.5 per cent alkali, filtering and washing, give the largest amount of organic matter extracted. A 5 per cent alkali solution extracts, under the same conditions, a somewhat greater amount of the α-fraction, but

TABLE 3

Amount of "humus" extracted from 100 gm. of soil with 5 per cent NaOH and 4 per cent NH_4OH from a Sassafras soil (A) and a clay soil (B)

SOIL	ALKALI USED	α-FRACTION	β-FRACTION
	mgm.	*mgm.*	*mgm.*
A	NaOH	565	1,473
A	NH_4OH	585	
B	NaOH	588	1,821
B	NH_4OH	570	

TABLE 4

Influence of alkali concentration (NaOH) upon the amount of "humus" extracted from a Sassafras sandy soil (100 gm. of dry soil used)

ALKALI CONCENTRATION	PERIOD OF EXTRACTION	α-FRACTION		β-FRACTION	
		Dry weight	Nitrogen content	Dry weight	Nitrogen content
per cent		*mgm.*	*mgm.*	*mgm.*	*mgm.*
2.5	30 minutes, pressure	910	25.3	1,507	21.2
5.0	30 minutes, pressure	1,060	20.6	1,560	22.7
10.0	30 minutes, pressure	832	13.6	630	4.3
2.5 + 2.5	60 minutes, pressure	895	23.1	2,688	33.8
5.0 + 5.0	60 minutes, pressure	1,038	18.8	1,895	23.4
5.0	48 hours, cold	987	....	1,475	....

of a lower nitrogen content. The greatest amount of nitrogen (56.9 mgm. from 100 gm. of soil) was extracted by the 2.5 per cent alkali repeated twice; a lesser amount was extracted by the single treatment with 2.5 per cent NaOH, and a still lesser amount by the single extraction with 5 per cent NaOH. A 10 per cent alkali solution extracted the smallest amount of the α-fraction with the lowest nitrogen content and only an inconsiderable amount of the β-fraction. This is due to the fact that the high concentration of sodium tends to coagulate the soil organic matter. A 5 per cent NaOH solution extracted in the cold a somewhat smaller amount of α and β-fractions than the same solute at a higher temperature.

To be able to determine the balance of the nitrogen in the soil and in the various fractions of "humus" obtained from the soil by treatment with 5 per cent NaOH, the same two soils that were used in the preliminary experiment were selected. The two soils were two plots of the soil fertility experimental series, treated in a like manner for the last 18 years. Every year 5A receives an equivalent of 16 tons of manure per acre, in addition to acid phosphate and potassium chloride, while 7A has received no fertilization during 18 years. Further information on these soils is given by Lipman and Blair (5). (Table 5.)

About 83 per cent of the nitrogen of the original soil is accounted for in the four fractions into which the soil organic matter is divided by the treatment with alkali:

1. The α-fraction contains about 25 per cent of the recovered nitrogen in soil 5A and about 19 per cent in soil 7A. 2. The β fraction contains about 20 per cent of the recovered nitrogen in 5A and about 33 per cent in 7A. 3. The solution from the β-fraction contains about 30 per cent of the nitrogen in 5A and 29 per cent in 7A. 4. The nitrogen left unextracted in the soil comprises about 24 per cent in soil 5A and about 19 per cent in 7A. Treatment of the soil with 5 per cent NaOH thus extracts 76 per cent of the nitrogen of a well manured soil and 81 per cent of an unmanured soil.

TABLE 5

"Humus" and nitrogen extracted with 5 per cent NaOH from a manured soil (5A) and a non-manured but cultivated soil (7A)

(On the basis of 100 gm. of dry soil)

SOIL	CONTENT OF ORGANIC MATTER, BY IGNITION	TOTAL NITROGEN IN ORIGINAL SOIL	α-FRACTION		β-FRACTION		NITROGEN IN SOLUTION FROM β	NITROGEN CONTENT OF RESIDUAL SOIL	TOTAL NITROGEN RECOVERED
			Yield	Nitrogen content	Yield	Nitrogen content			
	per cent	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	4.80	134	825	28.16	1,717	23.01	34.24	27	112.41
7A	2.78	74	318	11.66	1,840	20.33	18.36	12	62.35

The most interesting point in these results is the fact which tends to indicate the difference in the nature of the organic matter in the two soils. The ratios of the nitrogen and the organic matter content of the unmanured to the manured soils are 55.4:100 and 57.9:100 respectively; in other words, the organic matter in both soils, although different in quantity, has proportionally the same amount of nitrogen. On examining, however, the four fractions, in which the nitrogen and the organic matter are distributed, we find that the content of the α fraction and the water-soluble fraction is distinctly different in the two soils, whereas the amount of the β-fraction is practically the same, both in the amount of organic matter and in the nitrogen content.

These studies were repeated using a larger series of plots, under various treatments. (Table 6.) The results confirmed the observations made previously that differently treated soils belonging to the same soil type have about the same amount of organic matter and nitrogen in the β-fraction. The

differences are found largely in the α-fraction and in the amount of organic matter remaining in solution and not precipitated by the acid treatment. A comparison of the results obtained from those plots which receive stable manure year after year (5A, 18A and 5B) and from the two corresponding plots

TABLE 6

*"Humus" and nitrogen extracted with 5 per cent NaOH from a series of soils, under different manurial treatment**

(On the basis of 100 gm. of dry soil)

SOIL	TREATMENT	NITROGEN CONTENT OF SOIL	α-FRACTION		β-FRACTION			NITROGEN IN SOLUTION FROM β
			Yield	Nitrogen content	Yield	Organic matter	Nitrogen content	
		per cent	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	Manure	0.134	766	26.0	1,894	598	22.9	36.1
7A	Nothing	0.074	248	8.2	1,468	478	16.2	19.4
9A	$NaNO_3$ and minerals	0.097	438	15.6	1,688	526	17.5	31.8
11A	$(NH_4)_2SO_4$	0.095	434	14.2	1,833	585	18.2	33.4
18A	Manure, nitrate and minerals	0.132	792	21.8	1,831	579	19.0	37.8
5B	Lime and manure	0.128	674	23.0	1,702	556	19.8	41.8
7B	Lime alone	0.080	293	9.9	1,863	554	14.6	31.6
11B	Lime, $(NH_4)_2SO_4$ and minerals	0.078	456	14.0	1,785	539	18.0	37.8
19B	Lime and minerals	0.082	281	9.6	1,812	548	15.1	24.4

* See Lipman and Blair (5).

TABLE 7

"Humus" and nitrogen extracted from peat and muck soils with 5 per cent NaOH

(10 gm. of dry soil extracted twice with 50 cc. NaOH)

SOIL	α-FRACTION IN 10 GM. OF SOIL		NITROGEN LEFT IN SOLUTION
	Yield	Nitrogen content	
	gm.	*per cent*	*mgm.*
Humophous (English peat)	2.004	2.56	37.2
Peat No. 1754	2.131	3.12	67.4
Alphano muck	3.483	2.37	31.2
North Jersey muck	2.345	3.35	57.0
Florida muck	3.150	3.95	68.0
Muck No. 7	3.300	2.90	22.0
Forest black humous soil	3.980		
New Jersey peat, brown, uncultivated	4.060	2.10	70.6
New Jersey muck, black, cultivated, of same origin as preceding peat	4.350	1.85	57.8

which do not receive any manure or fertilizer (7A and 7B), shows that the residual effect of the manure results in a decided increase in the α-fraction of the soil or the "humic acids." Although no general conclusions may be drawn from these meagre results, some suggestion can be made here. The increase in

the α-fraction, as a result of the addition of organic matter, indicates its origin; the fact that the β-fraction is the same in one soil type, however differently treated, may be due to the fact that this is an adsorption compound and its amount depends on the amount of the absorbing agent, namely the aluminum, which may not vary in the same soil type.

The average nitrogen content of the "humus" or the α-fraction from an old peat soil was found to be 3.38 per cent. These and results from other experiments tend to indicate that the α-fraction of ordinary soil is very similar in nature and composition to the "humus" of peat and bog soils. The β-fraction of the various soils reported in table 6 shows a nitrogen content of 3.25 per cent for the organic part of these soils. The organic matter was determined by ignition, then allowance was made for the water lost by the inorganic part of the complex, assuming it to be entirely aluminum hydroxide.

To allow further comparison of the "humus" of ordinary soil and of peat soils, a series of analyses is given in table 7. The "humus" or α-fraction of peat and muck soils is very considerable, ranging from 20 to 35 per cent; the β-fraction was found to be present only in very small amounts. It is doubtful whether all the "humus" has been extracted from these soils. In some cases as little as 19 per cent of the original material was left in the residue. It is interesting to note that the three preparations having the lowest nitrogen content gave also the lowest amount of nitrogen in solution, after the α-fractions had been removed.

A black alkali soil (pH 9.8) examined for "humus" gave, per 100 gm. of dry soil, 112 mgm. of the α-fraction, containing 2.73 per cent nitrogen, and 1225 of the β-fraction, 70 per cent of which was ash, with 61 mgm. of nitrogen in the solution from β. In the nature of the organic matter, the alkali soil approaches normal soils.

To determine whether the nitrogen content of the α and β fractions is constant or can be changed by treatment with acids and alkalies, 2500 gm. of ordinary sieved field soil was extracted. It yielded 12,145 gm. of the α-fraction containing 2.84 per cent nitrogen and 1.2 per cent ash, and about 20 gm. of the β fraction, containing 1.08 per cent nitrogen. When 2-gm. portions of the dry material of the two preparations were boiled for 2 hours with 100-cc. portions of 2 per cent HCl, the α-fraction lost 19.5 per cent of the material, with 12.3 mgm. of nitrogen going into solution; in other words, the part that has become hydrolyzed contained only 3.15 per cent nitrogen or very close to the nitrogen content of the original preparation. The β-fraction lost 30.6 per cent, as a result of boiling with acid, and 7.7 mgm. of nitrogen went into solution, the hydrolized portion containing 1.26 per cent nitrogen, or also a trifle more than the original material. In other words, both preparations of soil "humus" are rather stable in composition, the amount of nitrogen being only inappreciably reduced by boiling with acids.

DISCUSSION

The determination of "humus" in soil was considered at one time to be one of the most important methods in soil analysis, but these determinations are now practically all abandoned. The proceedings of the Association of Official Agricultural Chemists show that where numerous determinations were made ten to fifteen years ago, none are made at present. This is due entirely to the fact that the results obtained by the methods in vogue were altogether too variable to be reliable. It is sufficient to quote Dr. J. H. Petit, who remarked at one of the meetings of the association that

> the results go far to confirm the idea that the determination of humus in soils is extremely unsatisfactory . . . . the determination of one definite constituent of soil organic matter as, for instance, carbon is a much better indication of what the soil contains.

The investigations presented in this paper were not undertaken with the idea of reviving the old methods of "humus" determination or of developing new methods. Since the very term "humus" does not stand for any definite chemical complex, one would expect a priori that any method suggested for measuring "humus" would have to be limited to one or more elements, such as carbon and nitrogen. If the term "humus," however, is limited to only that part of the soil organic matter which is resistant to rapid decomposition and if that complex (or only a definite part of it) can be measured by some convenient method, it is essential to investigate this method, before it can be utilized in a study of the origin of "humus" in the soil. As pointed out in the historical review, many of the recent investigators are inclined to consider lignins as at least one of the mother substances of soil "humus." Both of these have very similar properties in their behavior toward reagents. When lignin, prepared from natural organic substances by treatment with concentrated acids, is treated with an alkaline solution, only a part of the lignin, usually not more than 70 per cent, is brought into solution, even under pressure. The greater the concentration of alkali, the more continued the extraction and the higher the pressure, the greater will be the amount of lignin extracted. The same is true of soil "humus." A peat soil treated with gaseous hydrochloric acid was found to contain 70 to 75 per cent "lignin;" the same soil, on alkali extraction, gave only 40 to 45 per cent "humus;" in other words, this peat soil contains an organic complex, comparable to lignin in its chemical behavior and in its solubility in alkalies. In normal mineral soils, the quantity of "humus" is usually 1 to 6 per cent and one has to use the alkali extraction method, if the results thus obtained are comparable.

With these ideas in mind, the method of determination of "humus" in soils was studied. The results obtained are as follows:

1. The method finally adapted for the extraction of "humus" from the soil is fairly reliable, giving comparable results when the same soil is extracted at different times. It is sufficient to cite the results obtained from soil 5A, sampled at four different times of the year.

Three of these samples are reported in tables 1, 5, and 6. These results are 805, 825, 766 and 870 mgm. of the α-fraction for 100-gm. portions of dry soil, containing 23.91, 28.16, 26.0 and 28.2 mgm. of nitrogen, respectively. The results for the β-fraction vary more because of the high ash content of the latter. This points definitely to the fact that the particular method of measuring "humus" in the soil especially the α-fraction, or that part of the soil organic matter which is soluble in alkalies and precipitated by an excess of hydrochloric acid, deserves confidence and can be used for future studies. 2. There is great similarity between the α-fraction in normal soils and the "humus" of peat soils, especially in the case of muck and old peat soils. Fresh peat soils as well as forest "humus" soils contain much less nitrogen, the explanation for which is to be looked for in the origin of "humus" in the soil, as will be elucidated in the following contributions to this subject. 3. The existence of two fractions of "humus" in normal soils, both soluble in alkalies and precipitated by acids, one of which is insoluble in an excess of acid (α-fraction) and the other of which is redissolved (β-fraction). The first is practically free from ash, containing only 0.8 to 1.5 per cent ash, when properly washed with hydrochloric acid and water; the nitrogen content of the α-fraction is more or less definite ranging from 2.8 to 3.5 per cent. The β-fraction contains 50 to 70 per cent ash, depending upon the soil and only 0.8 to 1.5 per cent of nitrogen.

SUMMARY

1. Preliminary treatment of soil with hydrochloric acid before the extraction of "humus" with alkali is not required for the purpose of obtaining the maximum amount of "humus;" it may actually reduce the amount of organic matter which is extracted by the alkali.

2. Sodium hydroxide is preferable to ammonium hydroxide for the extraction of the "humus" from the soil. The amount of organic matter extracted is greater and the nitrogen content of this organic matter can be determined, without any danger of interference by the reagent.

3. It is proposed to carry out the determination of humus as follows:

The soil consisting of a mixture of several samplings is sieved through a 1-mm. sieve. Six 50-gm. portions of soil are placed in flasks or beakers and 50-cc. portions of 2.5 per cent NaOH solution are added. The flasks are then heated in an autoclave for 30 minutes at 15 pounds pressure or allowed to stand for 48 hours in the cold. The solution is then filtered through folded filter paper. Fresh 50-cc. portions of 2.5 per cent NaOH solution are added to the soil and extraction is repeated. The second extract is filtered through the same paper. The soil is then thrown upon the paper and washed first with 2.5 per cent NaOH solution, then two to three times with distilled water, until the solution comes through quite clear. The combined filtrate is then treated with 10 per cent warm hydrochloric acid, until a heavy precipitate is formed; half as much more acid is then added and the flask is well shaken. A part of the precipitate may go into solution. The precipitate left is filtered through a weighed dry filter paper or a Gooch crucible, washed several times with a 2 per cent solution of HCl, and then several times with distilled water. The precipitate is dried at 65 to 70°C. for 12 to 24 hours and weighed. Three portions of the precipitate are used for the determination of the ash content and three for total nitrogen determinations. The filtrate from the first precipitate is treated with a 2 to 3 per cent solution of NaOH, until a precipitate begins to form; the alkali is then added drop by drop to obtain the maximum precipitation, avoiding carefully an excess of alkali. This second precipitate (β) is also filtered through weighed dry papers or Gooch crucibles; the filtrate is carefully tested with a drop of acid and of alkali to see that no further precipitate is formed. If it does form, the filtrate is carefully adjusted again and the new precipitate is added to the first. This precipitate is

washed a number of times with distilled water, then dried at 90 to 100°C., and weighed. Two portions are used for ignition, two for total carbon, and two for total nitrogen determinations. The liquid from the β precipitate, which should be straw colored, should be used for the determination of total nitrogen and carbon in solution.

4. In the case of peat soils, only 5-gm. portions of dry soil are taken for analysis and treated with 50 cc. of a 5 per cent NaOH solution twice, as before.

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THE RELATION OF LIGHT TO SOIL MOISTURE PHENOMENA[1]

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PART I

INTRODUCTION

An attempt was made in this laboratory to measure the capillary or pressure potentials of soils by a vapor pressure method. The experiment was carried out by placing small cans of soil in desiccators containing solutions of known vapor pressure. These desiccators were immersed in a constant temperature water bath. It was hoped that by this method the vapor pressures of the soils could be determined and the pressure potentials calculated as will be explained in a later part of this paper. The results were disappointing because the wet soils in desiccators containing distilled water dried out far more than was expected.

After carefully considering all possible causes, the one that seemed to account best for this loss of water was that the soil, being a dark body, absorbed more light and heat radiations than the water, causing the soil to be maintained at a higher temperature. This difference in temperature would cause a distillation of water from the soil to the water in the bottom of the desiccator. Preliminary experiments carried out in this laboratory seemed to indicate that absorption of light was the big factor in the drying noted.

The only other cause that seemed reasonably to account for the drying, was that discussed by Washburn (11). He called attention to a drying of potters clays in damp chambers, and came to the conclusion that, since the clays were at a higher level than the water, the downward distillation was due to gravity. This conclusion was sustained by a preliminary experiment in which he supported wet clay balls in bottles. Some were over water and others were lowered into small open vessels sunk in water so that the clay was below the level of the water surrounding the inner vessel. He reported that the balls above the level of the water dried out, whereas those below the water level absorbed more water.

That this explanation is insufficient is proved by the fact that if a wick or column of soil is placed so as to connect the water and the dried clay ball, the ball will become wet. Water will distill from the wet ball to the free water below, and since the water that is distilled out will be replaced through the wick, there is a motion of water in a cycle. Without differences in temperature in the system this motion would violate the second law of thermodynamics, which states that a system or arrangement of matter operating in a cycle cannot transform heat into work in surroundings of constant temperature. There is, as Washburn concluded, some drying to be expected under isothermal conditions because of difference in height between the

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soil and water, but this is slight. Its magnitude will be discussed in a later part of this paper.

The present paper reports: (*a*) experiments designed to determine the effect of light on soil moisture phenomena, and (*b*) a theoretical study of the mechanics of soil moisture, especially in its relation to saturated vapor under varying conditions of light. The theoretical part considers the effect of light on the moisture equilibria between the opaque and transparent portions of the systems considered.

EXPERIMENTS CONDUCTED

Description of absorption apparatus

To determine just what effect light has on absorption of water vapor by dry soils and distillation from wet ones, a special apparatus was built. It was submerged in a large water bath held at constant temperature by a non-incandescent electric heater controlled by the system described by Thomas (8). By this method the temperature could be held within a range of 0.002°C. as long as the electric power was continuous. The water in the bath was well stirred to insure uniform temperature throughout.

The apparatus (fig. 1) consisted of a 10-inch desiccator with a plate glass top. In the top were drilled one ¼-inch hole in the center to allow for the stirrer shaft, and six equally spaced ¼-inch holes on the circumference of a circle of 3½-inch radius. In the center hole was sealed a short piece of glass tubing to act as a bearing. Through this was inserted the stirrer shaft carrying a fan for stirring the air, the shaft being bent so as to stir the water. In each of the six holes was sealed a 4-inch piece of glass tubing. Soils to be tested were placed in the lids of standard 3-inch aluminum soil cans suspended on fine copper wires through these tubes. A balance sensitive to 1 mgm. was mounted above the desiccator on a movable horizontal platform, and a fine chain was suspended from the left pan through a hole in the balance case, and was counterbalanced by a weight on the right pan. With this arrangement it was possible to bring the balance over each hole in succession, obtain the direct weight of the soils, and from this calculate their moisture percentages. This could be done at any time without opening or moving the desiccator. On the top of each of the six glass tubes, a short piece of rubber tubing was placed so that except when weighings were being made, each hole was stopped with a glass plug, entirely sealing the desiccator.

The advantage of stirring the air and water, as reported by Wilson (13), is that it requires only about one-tenth to one-twentieth the time to reach equilibrium with stirring as without it, although the stirring does not in any way displace the equilibrium point.

Soils used; methods

Three different washed soils were used for the experiment: Greenville silty clay loam; Trenton clay, a heavy clay soil; and T_7, a separate of Trenton clay of sizes less than 0.3μ in radius. These soils have been used for other experiments at this station and their mechanical analyses and vapor pressure-moisture percentage curves are reported by Thomas (9).

The experiment was started using two approximately 5-gm. samples of each kind of soil, one relatively dry and the other approximately saturated. The data are presented almost entirely in the form of moisture percent-time curves, as they are too cumbersome in the tabular form. To determine the accuracy of the data, on several occasions after the weighings were made they were repeated, and in no case did the differences noted amount to a difference of 0.1 per cent in moisture content. All moisture percentages are expressed on the dry-weight basis as determined by heating samples of the soil to 110°C. for 24 hours. Figures 2, 3, and 4 show the results obtained in chronological order. The discontinuities were the result of needs for repair of some parts of the apparatus, so the data of the different figures cannot be connected up.

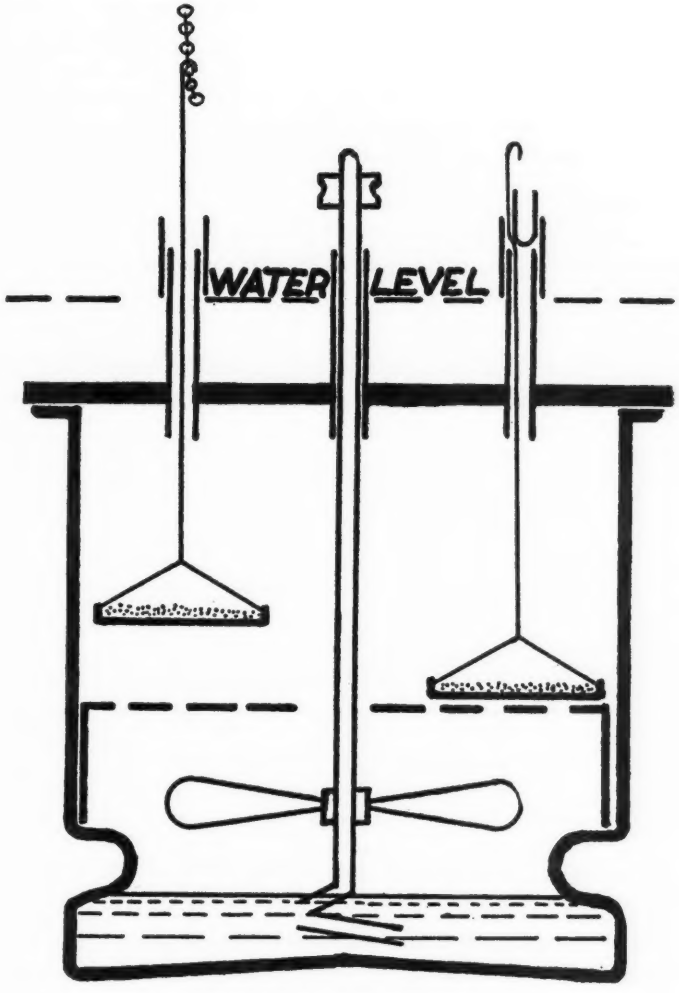

FIG. 1. DIAGRAM OF APPARATUS

The pan on the left is shown in the weighing position, connected to the chain supported from the balance (balance not shown). The pan on the right is in the position in which it is left during the absorption, and the hole in the top is plugged.

Discussion of data

Period 1. In figure 2 are shown the results obtained without absolute darkness. The walls and bottom of the bath were opaque but the top was not entirely covered. The curves became nearly horizontal by the fifteenth

day. At this time the stirrer in the apparatus was stopped and for the remaining 5 days the absorption was practically zero, and the drying was greatly reduced.

Period 2. When the apparatus was again started (fig. 3) a test was made for 6 days to see that everything was in good repair. On the fourth, fifth, and tenth days, because of trouble with the electric power, the temperature fluctuated but for the remainder of the period the power was continuous as shown by a recording instrument.

On the sixth day a 200-watt type-C lamp equipped with a reflector was placed about 50 cm. above the apparatus. In one day all the soils except the

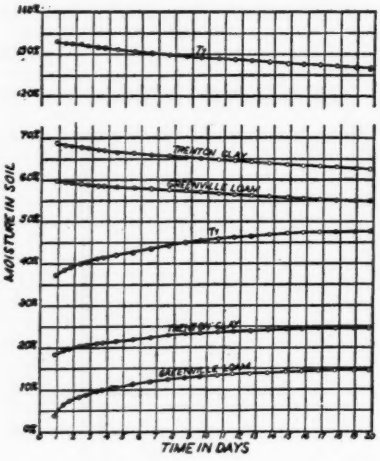

FIG. 2

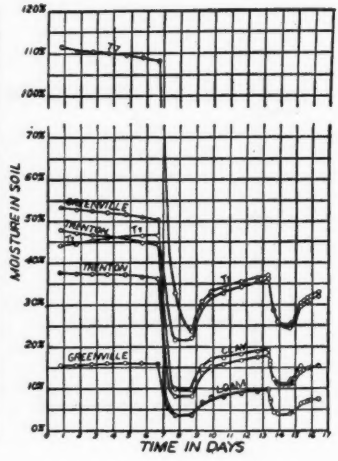

FIG. 3

FIGS. 2 AND 3. MOISTURE TIME CURVES OF THE SOILS IN SATURATED ATMOSPHERE

Figure 2 shows the wetting and drying curves in very subdued light.

Figure 3 shows the effect of strong light in the desiccator, from sixth to eighth and the thirteenth days.

wet T_7 had reached approximate equilibrium, this had lost 3.3 gm. of water reducing its moisture content 75.5 per cent. By the next day all had reached equilibrium. The samples of the clays that had been saturated did not dry as much as those that had been only moist. This was as expected, especially with the heavy soils, as saturating tends to pack the soil closer together and thus allows it to hold a greater amount of water at a given vapor pressure of the soil. This effect was reported by Thomas (9).

On the eighth day the light was turned off and the soils immediately began to absorb water. On the thirteenth day the light was turned on again, left one day, and turned off. Table 1 shows the moisture percentages at selected times during period 2, and compares these with the values of the so-called

hygroscopic coefficient and the wilting coefficient, as determined by standard methods.

These results show that soils will absorb enough water from a saturated atmosphere to bring their moisture contents to values in excess of twice their "hygroscopic coefficients" and to values greatly in excess of their "wilting

TABLE 1

Per cent of moisture in soils under various conditions of light during period 2, compared with "hygroscopic coefficient" and "wilting coefficient"

	GREENVILLE LOAM		TRENTON CLAY		T_7	
	Wet	Dry	Wet	Dry	Wet	Dry
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
"Hygroscopic Coefficient"	6.30	6.30	10.2	10.2	*	*
"Wilting Coefficient"	9.30	9.30	15.0	15.0	*	*
Sixth day, before light was turned on	50.40	15.80	44.2	36.1	108.2	46.5
Eighth day, light on two days	3.74	3.60	9.6	8.1	23.6	22.1
Thirteenth day, light off for five days	9.90	9.50	19.3	17.9	37.0	36.2
Fourteenth day, light on for one day	4.40	4.50	12.2	11.2	25.8	25.2
Sixteenth day, light off for two days	7.50	*	*	15.4	32.9	31.9

* Data not available.

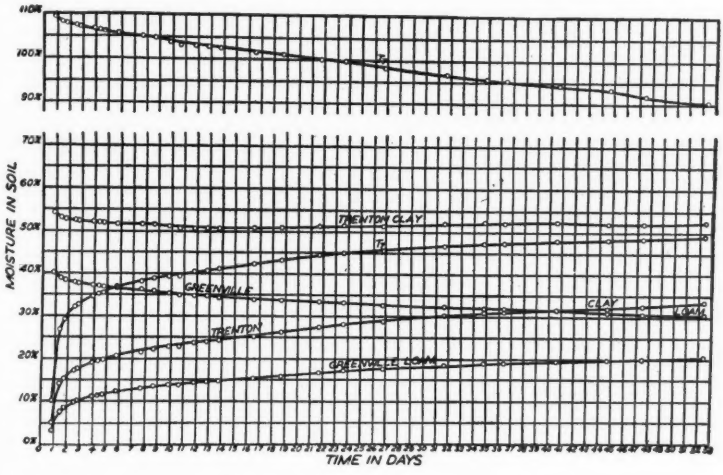

FIG. 4. MOISTURE TIME CURVES OF THE SOILS IN SATURATED ATMOSPHERES
Wetting and drying curves under conditions of less light than in figure 2

coefficients." They show further that in the presence of light a wet soil will dry in a saturated atmosphere to values near or below its "hygroscopic coefficient," and when light is excluded will absorb moisture again.

In this experiment the way in which the moisture content varied with light

intensity leaves little doubt as to the relationship between these two quantities, because as nearly as possible all conditions except light were the same as those during period 1 and the first 6 days of period 2.

Period 3. Since from the theory of radiation, all bodies, regardless of color, enclosed in a constant and uniform temperature opaque shell, are at the same temperature, an attempt was made to realize this by enameling the desiccator and covering the bath more completely. The results (fig. 4) were only partially satisfactory because the enamel peeled off opposite the T_7 samples and let considerable light in. That the lower light intensity in the desiccator allowed more rapid absorption of water vapor can be seen from the values of the slopes of the two sets of wetting curves at corresponding moisture percentages. The period taken was from the ninth to the fourteenth days of period 1, and the corresponding range in moisture percentage during period 3. The time chosen from period 1 was the last 5 days before the stirrer was stopped. The slopes are given in table 2.

At the end of period 3 the apparatus was enclosed in a metal case and started again but the power became so irregular that the experiment had to be discontinued.

TABLE 2

Slopes of the wetting curves in selected range, taken from figures 2 and 4

Expressed in per cent increase per day

CURVES FROM	GREENVILLE LOAM	TRENTON CLAY	T_7
Fig. 2, period 1. Desiccator transparent	0.29	0.22	0.36
Fig. 4, period 2. Desiccator enamelled	0.43	0.45	0.36*

* Enamel peeled off opposite the T_7 samples, letting light in.

Calculation of temperature of soil on eighth day of period 2

By using the data of table 1 and the vapor pressure-moisture percentage curves obtained by Thomas (9), some interesting calculations can be made. To illustrate the method of calculation of the temperature of the soil when the lights were turned on, one set—that for the wet Trenton clay—will be calculated in detail. From table 1 the moisture percentage after the light had been on for two days was 9.6 per cent, which according to the curves just referred to (drying curve) would have at this moisture percentage about 84 per cent of its maximum vapor pressure. The vapor pressure of water at 25°C., the temperature of the bath, is 23.78 mm. of mercury. Since the warm soil was in vapor equilibrium with the water at 25°C., its vapor pressure must have been the same, and from the vapor pressure data this was only 84 per cent of its maximum. So its maximum vapor pressure must have been $\frac{23.78}{0.84} = 28.30$ mm. This vapor pressure for a saturated soil or for water would be reached at a temperature of 27.95°C. or 2.95°C. warmer than the water in the same

desiccator. Comparison of the other wet soils with their corresponding vapor pressure curves (drying curves) shows that they were at the same per cent of their maximum vapor pressure, and thus at the same temperature. Similar calculation cannot be made for the dry samples, as their previous history was partial saturation and then drying, for which detailed vapor pressure data are unavailable. The curves would be expected to fall between the curves for wetting dry soil and drying wet soil. In every case the range of moisture percentage allowed for 84 per cent vapor pressure between the wetting and drying curves included the value of the corresponding dry sample, on the eighth day.

Direct measurement of temperature of soil in light

As a result of the close checks obtained by the calculations there was little doubt as to their accuracy. To make sure that such differences in temperature could exist in a desiccator immersed in a constant temperature bath, a can of saturated Trenton clay soil was placed in a 5-inch desiccator containing water, and a thermocouple sensitive to 0.2°C. was connected with one juncture in the soil and the other in the water in the bottom of the desiccator. A 200-watt type-C lamp with reflector was mounted 50 cm. above the top of the desiccator, which was 5 cm. below the surface of the water. The temperature of the soil reached a value 4.5°C. warmer than that of the water as compared with 3.0°C. warmer in the previous experiment. This smaller difference in temperature was due to the fact that the tubes in the top of the large desiccator were sealed into the lid with wax, rendering opaque a considerable part of the top.

After the reflector was removed, the soil was found to be only 0.5°C. warmer than the water. A calculation, just the reverse of the one used for the temperature of the soil, based on the wetting curve since the soil had been dried by light, showed that the soil should have had 13.5 per cent water, whereas a direct determination showed 12.9 per cent. The difference is well within the experimental error.

The thermocouple was then replaced by one sensitive to 0.04°C., and the desiccator exposed to the laboratory light. The experiment was conducted during February in a laboratory with a north exposure. During the day the difference in temperature between the soil and water was from 0.10° to 0.16°C. while at night this difference was reduced to practically zero.

CONCLUSIONS

1. Soils at the moisture content corresponding to the "hygroscopic coefficient," as determined by present methods, will continue to absorb large amounts of water when exposed to a saturated atmosphere in a dark constant temperature chamber. The amount that the soil will absorb is in excess of the moisture content at the "wilting coefficient."

2. The equilibrium point reached under any but isothermal conditions is a function of the light intensity in the apparatus containing the soil.

3. Laboratory light is sufficiently intense to cause serious differences in temperature between transparent and dark bodies.

Part II. Theoretical Discussion

Mechanics of soil moisture

The hygroscopic coefficient has been usually considered an equilibrium point: the maximum percentage of water vapor that can be absorbed from a saturated atmosphere. As ordinarily determined the value is about 0.75 of the wilting coefficient.

Bates and Zon (1) and also Robinson (6) reported that it was impossible to obtain equilibrium at relatively low moisture contents. Both accounted for this on the assumption that dissolved substances in the soil solution lower the vapor pressure of the soil below that of free water, and as a result there can be no equilibrium as long as there is any free water at the same level.

In case there are no dissolved substances in the soil solution the problem is different. This condition can never be reached but is approached very closely in washed soils. Various investigators have tried both experimental and theoretical methods to determine under what condition or conditions a soil can be in equilibrium with a saturated water vapor. The results in many cases are contradictory, indicating that in their investigations some essentials have been overlooked.

Saturated soil in equilibrium with saturated vapor

The deduction of the equilibrium point from the amount of liquid water absorbed by a soil in direct contact with water can be made as follows:

> If liquid water and its vapor are in a closed container at constant temperature, the water will distribute itself through the contents according to the laws of hydrostatics. Water will rise in capillary tubes, near solid objects, and also in open spaces between particles of soil. When equilibrium is reached in the liquid phase there must also be vapor equilibrium, for if there were not, water would evaporate at one place and condense at another, thus destroying the liquid equilibrium, and the water would flow back. This would be a motion of water in a cycle, which cannot take place under isothermal conditions. If some of the liquid should become detached, vapor equilibrium would not be reached until all conditions were just the same as if there were liquid communication. If this were not true, after the vapor had come to equilibrium a water connection could be made and there would be a flow of water. This would destroy the vapor equilibrium and there would be a motion of water in a cycle, which is impossible. Presence of air in the system will in no way affect the final equilibrium point but will retard the movement of vapor.

This conclusion was reached by Sir William Thomson (10) who states,

> Detached portions of the liquid in separate vessels all enclosed in one containing vessel cannot remain permanently in any other relative positions than those they would occupy, if there were hydrostatic communication of pressure between the portions of the liquids in the several vessels.

It is a well known fact that water will rise in soils and practically saturate them for considerable heights. When equilibrium is reached the soil at any level in addition to being in liquid equilibrium with the water below is also in vapor equilibrium. From this it is safe to say that complete saturation is one condition of the soil for vapor equilibrium between a soil and a saturated atmosphere.

The absorption experiments reported in this paper indicate that there is equilibrium between a saturated vapor and saturated soil. None indicate that there can be equilibrium between relatively dry soil and saturated vapor as some workers have reported. Although the experiments did not indicate a second equilibrium point they did not prove its non-existence, but indicate that if one exists it must be very unstable.

Effect of differences in height on equilibrium

In these absorption experiments the soils were about 10 cm. above the water level in the desiccator. As indicated before, this would tend to make the final equilibrium a little dryer than saturation. Since, when vapor equilibrium is reached, the soil must have the same moisture content it would have if connected with a wick to free water below, the size of pores that can be filled at this height can be calculated. The radius of a tube or pore that can support a column of water of any height h is given by the formula for rise of water in capillary tubes: $r = \frac{2T}{hg}$; where T is the surface tension of water, 72.1 dynes per cm. at 25°C.; r is the radius of the tube or pore; and g is the acceleration of gravity.

$$r = \frac{2 \times 72.1}{10 \times 980} \qquad r = 0.01471 \text{ cm.}$$

Then a pore of 0.1471 mm. radius or 0.2942 mm. diameter would support a column of water 10 cm. high. This means that at this height above a free water surface a soil with no pores larger than 0.2942 mm. would be completely saturated.

Derivation of equilibria by geometry and mechanics

Previous studies. Since conclusive proof by experimental methods is difficult, attempts have been made to deduce the equilibrium point by geometry with the aid of mechanics. To do this, it must be assumed that the soil is composed of uniform, insoluble spheres, regularly packed. Wilsdon (12) on these assumptions attempted to calculate the moisture percentage of the spheres when in equilibrium with a saturated vapor. His paper was reviewed, part of the mathematics copied, and a discrepancy pointed out by Keen (4).

Wilsdon started his analysis by considering the water wedge between two equal spheres. He further assumed that the section of the surface of the water

wedge, S (fig. 5) would be the arc of a circle tangent to the two circles A and B. Since the curvature of any surface is the algebraic sum of the curvatures taken on two mutually perpendicular planes normal to the surface at the point in question, the curvature of the water surface will be:

$$c = \frac{1}{r_2} - \frac{1}{r_1} \qquad (A)$$

The surface of the wedge must have constant curvature since all parts are in equilibrium hydrostatically. The condition that the wedge be in equilibrium with a saturated vapor is that the surface shall have zero curvature. This condition will be reached when r_2 equals r_1. By using this condition Wilsdon calculated the central angle 2θ, subtended between the point of contact of the two spheres and the point of tangency of the wedge, to be 53° 6′. Assuming the closest possible—tetrahedral—packing each sphere would touch twelve

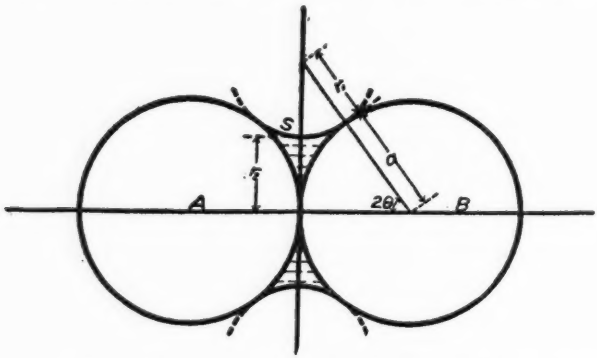

FIG. 5. SECTION THROUGH THE CENTERS OF TWO SPHERES SHOWING WATER WEDGE WITH CIRCULAR SURFACE SECTION

others. By calculating the number of spheres as a function of the radius in 100 gm. of soil, and remembering that there are six water wedges for each sphere in the mass, and knowing the volume of each wedge, he found that the moisture at equilibrium would be 23.95 per cent, which would be independent of the size of the spheres. This value he attempted to correlate with the 21 per cent in the Briggs-Shantz Formulae (2). Keen (4) objected that in any possible regular packing of spheres there would be an overlapping of water wedges before the condition of zero curvature is reached. Thus to an extent Wilsdon's analysis is invalidated. Keen made no attempt to describe the conditions after overlapping.

Calculation assuming catenoidal surfaces. The assumption that the surface of the water, S, is the arc of a circle, leads to a considerable error in calculating the angle 2θ and the volume of the wedge. The surface of a water film of zero curvature between two spheres can be

shown by mathematics to be a catenoid (a catenary revolved about its directrix). The equation of the catenary with the directrix as the X-axis and the axis of symmetry, the Y-axis is:

$$y = C \cosh \frac{x}{C} \tag{B}$$

where by definition

$$\sinh u = \tfrac{1}{2}(e^u - e^{-u}) \tag{C}$$

and

$$\cosh u = \tfrac{1}{2}(e^u + e^{-u}) \tag{D}$$

and where C is the Y-coördinate of the vertex of the catenary. Before the volume of the wedge can be calculated, the angle of contact between the water and soil must be known. Since for many such substances as glass and quartz the angle of contact is zero or nearly so it will be assumed that the same holds for the soil; that is, that the surfaces of the water and of the soil particle are tangent at the point of contact. With this assumption all that is necessary to evaluate C of equation (B) is to solve the equations of the catenary and of one of the circles for tangency; that is, equate the values of y and the values of the slope, or $\frac{dy}{dx}$.

The equation of a circle of radius a tangent to the Y-axis at the origin is:

$$x^2 - 2ax + y^2 = 0 \tag{E}$$

or

$$y = \sqrt{2ax - x^2} \tag{F}$$

Differentiating (B)

$$\frac{dy}{dx} = \sinh \frac{x}{C} \tag{G}$$

Differentiating (F)

$$\frac{dy}{dx} = \frac{a - x}{\sqrt{2ax - x^2}} \tag{H}$$

Equating the values of y from (B) and (F)

$$\sqrt{2ax - x^2} = C \cosh \frac{x}{C} \tag{I}$$

Equating the values of $\frac{dy}{dx}$ from (G) and (H)

$$\frac{a - x}{\sqrt{2ax - x^2}} = \sinh \frac{x}{C} \tag{J}$$

These solved graphically give the following values:

$$\left.\begin{aligned} C &= 0.6815\ a \\ x &= 0.4356\ a \\ y &= 0.8255\ a \end{aligned}\right\} \text{(coordinates of the point of tangency)}$$

$$2\theta = 55^\circ\ 38'$$

By integration, the volume of water wedge is found to be $0.463\ a^3$. Assuming, as Wilsdon did, the six independent contacts per particle without overlapping, the moisture would be 27.63 per cent, or 4.19 per cent more than by assuming the arc of a circle; or by assuming the arc of a circle, only 85 per cent of the true value is obtained.

Relationship with other water wedges. With cubical packing when the angle 2θ becomes 45°, and with tetrahedral packing when 2θ becomes 30°, the water wedges will overlap, so that the analysis breaks down as pointed out by Keen. The question then arises as to the possibility of an equilibrium point after the wedges overlap and before saturation is reached. Assume

that each sphere is surrounded by six others equaly spaced as in cubical packing; and that the water wedges could expand, independent of the others, until each comes to zero curvature. At this condition each wedge would have spread 55° 38′ from each point of contact of the spheres, and since these points of contact are 90° apart, wedges on the line between two contacts would overlap 21° 16′. This condition would be unstable since adjacent wedges if they had expanded independently would intersect at an angle less than 180°, which would smooth out leaving a negative curvature, and not a zero curvature as Wilsdon assumed.

All spheres covered before zero curvature. Assuming the loosest possible—cubical—packing there are six contacts on each sphere and these are at the intersections with the surface of the sphere of three mutually perpendicular lines from its center. Take any three of the mutually perpendicular lines from the center to the surface as the positive X, Y, and Z axes, and a line between, such that its direction cosines, l, m, and n are positive and equal. The point where this line intersects the surface of the sphere will be equidistant from the points where the axes intersect the surface. The value of m can be determined, since the sum of the squares of the direction cosines equals unity:

$$l^2 + m^2 + n^2 = 1 \qquad (K)$$

$$l = m = n \qquad (L)$$

From (K) and (L)

$$3m^2 = 1 \qquad (M)$$

$$m^2 = 0.3333 \qquad (N)$$

$$\log m = 9.7614 - 10 \qquad (O)$$

$$\cos^{-1} m = 54° 44' \qquad (P)$$

Since for zero curvature the angle $2\theta = 55° 38'$ is greater than $\cos^{-1} m = 54° 44'$, if the six water wedges should expand independently to zero curvature the entire sphere would be covered and, as previously shown when the angles smoothed out, there would be negative curvatures.

No equilibrium until saturation. Between this condition and saturation there will be only air-water surfaces of constant curvature to consider, since all the spheres are covered and it is easily shown that the containing walls would be covered. Since there is air in the soil practically bounded by water, there must be negative curvatures somewhere, and since the curvature must be constant throughout, it must be negative everywhere. There must be negative curvature somewhere since it is obviously impossible to bound a pocket of air with a surface that has everywhere a positive curvature on the air side.

Application to actual soil. It is very probable that in practice there would be air trapped in pockets in the soil, but since the air would be bounded by a water surface of negative curvature, it would be under greater pressure than the air outside. Since the solubility of air varies directly with the pressure, the trapped air would slowly dissolve and diffuse out of the soil.

Although the previous discussion holds rigorously only for uniform spheres regularly packed, it should hold fairly well for an actual soil. Soil particles are of variable size and shape but it is reasonable to assume that their contacts are as close as would be the case with spheres packed in the loosest regular condition possible.

Since the experiments reported in Part I of this paper indicate that only when saturated is a soil in equilibrium with saturated vapor, and since a theoretical analysis shows that, at least with uniform spheres under the above conditions, an equilibrium point dryer than saturation is impossible, it seems evident that one does not exist, and that previous workers have failed to reach an isothermal equilibrium with pure water.

Effect of light on soil absorption and other experiments

The above analyses do not hold when light is allowed in the apparatus. As was shown in figure 3, when light was turned into the desiccator the soils dried out very markedly. Table 3 based on calculations from the vapor pressure curve of Trenton clay shows the magnitude of the changes in moisture content which will result in a closed vessel from certain differences in temperature between soil and water.

Since in the author's experiments differences in temperature of 0.16°C. between transparent and opaque bodies were noted in winter in a laboratory with a north exposure, it is evident that it is important to conduct absorption experiments in the dark.

Not only are soils experiments affected by light, but also other constant temperature experiments where opaque objects are surrounded by glass and placed in a thermostat. In such cases the difference in temperature between

TABLE 3

Relation of difference in temperature between soil and water in a closed chamber to the moisture content of Trenton clay

DIFFERENCE IN TEMPERATURE OF SOIL AND WATER	VAPOR PRESSURE IN PER CENT OF MAXIMUM	MOISTURE IN SOIL
°C.	*per cent*	*per cent*
0.87	95	12
0.34	98	17
0.00	100	34–52*

* Values obtained experimentally. The dry sample absorbed 34 per cent by the end of period 3 (fig. 4), in a saturated atmosphere. As sample was not in absolute darkness and it was still absorbing water when the absorption was stopped, this value would be well below equilibrium value. At the same time under the same conditions, the wet sample contained 52 per cent of water and seemed to be approximately at equilibrium. This value is then probably more nearly correct than 34 per cent.

the opaque and the transparent bodies might be many times greater than the temperature fluctuations allowed in the thermostat. The theory of radiation indicates a means of avoiding trouble from light, since it shows that all bodies, regardless of shape or color, inside of a constant temperature opaque shell, will be at the same temperature.

Since the vapor pressure data of Thomas were used in calculating temperatures of soils in light it might be well to point out that these data were practically free from any light effect. Two methods were used: the dynamic, in which the soils were placed in brass tubes in a thermostat; and the static, in which the soils were placed in desiccators. The latter were placed in well insulated boxes and stored in a dark cellar. The temperature in the cellar would vary not more than 0.2°C. in a week.

Effect of fluctuations in temperature. Accurate temperature control in absorption experiments is necessary since dew will be deposited on cooling and

the air will become unsaturated on warming. Since the heating and cooling take place at the outside of the apparatus first, there is a great possibility that the net effect of temperature fluctuations would be a one-way distillation of water displacing the equilibrium point. Many places on the curves (fig. 2, 3, and 4) where points fall below the smooth curve, correspond to a failure of the power or of the control to operate properly. Such places are: figure 3, the fifth, sixth, and tenth days; and figure 4, the eleventh day.

Effect of light on mechanical stresses in soil moisture. The effect of light on the moisture of soil in a saturated atmosphere may not appear large from the standpoint of vapor pressure or moisture percentage, yet when considered from the point of view of the forces set up when dried soil is connected with free water, the effect of light is enormous.

Definition and discussion of potential. In order to calculate these forces it will be necessary to give a general review of the meaning of potential,[3] the various potentials used, and the methods of calculating them.

In a singly connected, conservative force field the potential at any point is the amount of work required to move unit mass from an arbitrarily chosen point of zero potential to the point in question. If **f** as a vector is the force on unit mass and $d\mathbf{s}$ an infinitesimal vector along the path then the potential at a given point B will be:

$$W = \int_A^B \mathbf{f}\, d\mathbf{s} \qquad (Q)$$

where A is the arbitrarily chosen point of zero potential. If there is no force in the field; that is, if there is equilibrium, the potential will be constant throughout.

In case more than one force field operates in a region the potential for each field and the potential due to the resultant field or total potential can all be calculated by equation (Q). The potential at a point is independent of the mass present and is the work that would be required to move unit mass from the point of zero potential to the point in question.

Calculation of forces when potentials are known. If the total potential is known throughout a region the net force per unit mass causing motion will be given by the negative gradient of the potential at any point. The average net force per unit mass between two points will be given by the difference in potential divided by the distance between the points and directed from high to low potential.

Units. In absolute units, which are used for formulae in this paper, potentials are expressed in dyne-centimeters per gram, written briefly dyne-cm./gm. Since the above units are small for some work it is convenient to express potentials in gram-centimeters per gram (gm. cm./gm.) or in cubic centimeter-atmospheres per gram (cc.-atm./gm.). The relations between these units are given by the following:

$$1 \text{ cc.-atm./gm.} = 76 \times 13.6 \text{ gm.-cm./gm.} = 1034 \text{ gm.-cm./gm.} \qquad (R)$$

$$1 \text{ gm.-cm./gm.} = 980 \text{ dyne-cm./gm.} \qquad (S)$$

Potentials used. Gravitational potential. In this discussion four potentials will be used frequently, they are: (a) the gravitational potential indicated by φ, (b) the pressure potential indicated by π, (c) the osmotic potential indicated by ω, and (d) the sum of these three the total potential, Φ, given by the equation:

$$\Phi = \varphi + \pi + \omega \qquad (T)$$

[3] A complete discussion of potential functions can be obtained in Mathematical Theory of Electricity and Magnetism, by Jeans; in The Theory of Electricity and Magnetism, by Webster; in An Introduction to Mathematical Physics, by Houstoun; or in any other good treatise on mathematical physics.

Zero gravitational potential is taken where convenient, and in absolute units has a value of gh, where g is the acceleration of gravity and h is the distance above the level of zero gravitational potential

$$\varphi = gh \qquad (U)$$

Pressure potential. The pressure potential is the potential due to the internal stress of the material. The pressure potential, π, at a point B is given by the integral.

$$\pi = \int_A^B \frac{dp}{\rho} \qquad (V)$$

where A is at the arbitrarily chosen point of zero pressure potential, p is the pressure in dynes per sq. cm. and ρ is the density. When liquid water is considered, ρ is constant and equal to unity; therefore the value of the integral becomes numerically equal to p, and dimensionally equal to $\frac{p}{\rho}$. Ordinarily the point of zero potential is taken at zero hydrostatic pressure, making the potential zero at a free flat surface of a liquid. Since the pressure beneath the surface

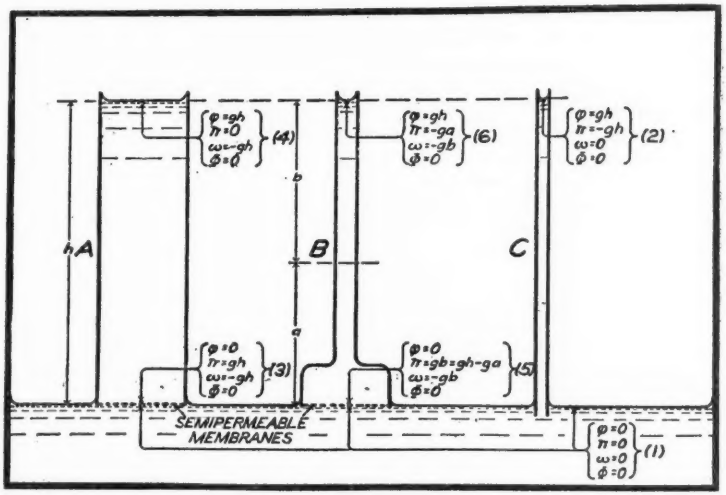

FIG. 6. DIAGRAM SHOWING THE RELATIONSHIPS BETWEEN THE VARIOUS POTENTIALS IN AN EQUILIBRIUM SYSTEM

(For description see text)

of a liquid is $-h\,\rho g$, where h is the vertical distance, positive upwards, from the free flat surface of the liquid to the point in question; and g is the acceleration of gravity. Then

$$\frac{p}{\rho} = -\frac{h\rho g}{\rho} = -hg = \pi \qquad (W)$$

π is defined by equation (V) as it was by Silberstein (7), and is used because it includes both positive and negative pressures and is valid through varying densities. Some previous writers on soil moisture have used two potentials, the hydrostatic pressure potential in the regions of positive pressure and the capillary potential in regions of negative pressure. Since the only difference between the two is one of sign, the one potential π as defined will be used here to include both.

Osmotic potential. The osmotic potential, ω, of a solution is the work necessary to transport unit mass of water through a semipermeable membrane from pure water to the solution, against osmotic forces. By definition, pure water is at zero osmotic potential. As will be shown later the osmotic potential of solutions is negative.

Interrelations of potentials in equilibrium system. With the aid of figure 6 the relationships between $\pi + \omega$ and vapor pressure can be derived. In a closed vessel are the following: C, a capillary tube of such a diameter that water will rise in it to a height h above the free surface of the liquid; A, a large tube with a semipermeable membrane on the bottom and filled with a uniform solution of such strength that the liquid will rise to a height h; and B, a capillary tube of such diameter that it will lift water to a height a, and filled with a solution of such concentration as to raise the solution a height b, with the further condition that $a + b = h$. This would make the top of the liquids in the three tubes the same height. The closed vessel with air removed contains a system of water, its vapor and solutions.

If the entire system is brought to isothermal equilibrium there can be no movement of liquid or vapor in cycles. Throughout the liquid phase the total potential must be constant, because if not there would be unbalanced forces causing motions in the system. π and ω have already been defined as zero at the free flat pure water surface, so for convenience φ will also be arbitrarily chosen as zero, making the total potential Φ zero. Since Φ is constant, the total potential is zero throughout the liquid phase.

Since:

$$\varphi = gh \qquad (U)$$

$$\pi = -gh \qquad (W)$$

and

$$\Phi = 0 \qquad (X)$$

ω can be calculated throughout the system.

As was previously stated at the free flat water surfaces, positions (*1*) (fig. 6) all the potentials are by definition zero. In the water at the top of the capillary tube, position (*2*), $\omega = 0$ by definition; $\varphi = gh$ (*U*); and $\pi = -gh$, (*W*).

In tube *A* just above the membrane, position (*3*), $\varphi = 0$ because it is at $h = 0$; $\pi = gh$ by (*W*) since the point is a distance h below the free surface of the liquid in the tube; and since $\Phi = 0$ in the liquid, ω must be $-gh$. At the surface of the liquid in the tube the pressure potential is zero, $\varphi = gh$, and since Φ is zero, $\omega = -gh$. Since the concentration is the same at the top and bottom of the tube it would be expected that the value of ω would be the same at both places. It can also be seen that its value is given by:

$$\omega = -gh \qquad (Y)$$

where h is the height to which the solution will rise in a large tube by osmosis through a semipermeable membrane.

Just above the membrane in tube *B*, the gravitational potential would be zero; $\omega = -gb$ (*Y*) since the solution is concentrated enough to rise to a height b; and since the total potential is zero, $\pi = gb = gh - ga$, because $a + b = h$. At the surface of the liquid in the tube the osmotic potential would be the same as at the bottom; $\varphi = gh$ (*U*); and since $\Phi = 0$, $\pi = -gh + gb = -ga$.

It is important to note that the sum of the osmotic and pressure potentials at the top of every tube is the same and equal to $-gh$, and that these three surfaces are in equilibrium with the vapor at the same vapor pressure. As shown by the above where there is a combination of capillary and osmotic potentials present the following equation holds:

$$\pi + \omega = -gh \qquad (Z)$$

where h is the height above the level of a free flat pure water surface in isothermal equilibrium.

Relationship between $\pi + \omega$ and vapor pressure. The relationship between $\pi + \omega$ in the liquid and the equilibrium vapor pressure can now be developed.

The pressure p of a vapor at height h above a free flat pure water surface, is given by the exponential equation:

$$p = p_o\, e^{\frac{-p_{vo}}{p_o} gh} \qquad (A_1)$$

Where p_o and ρ_{vo} are the vapor pressure and density respectively at the free flat pure water surface,
Solving (Z) for h:

$$h = -\frac{\pi + \omega}{g} \qquad (B_1)$$

Substituting value of h from (B_1) in (A_1):

$$p = p_o\, e^{(\pi+\omega)\frac{\rho_{vo}}{p_o}} \qquad (C_1)$$

Transforming (C_1) to logarithmic form where ln stands for natural logarithms, that is, to the base $e = 2.7183-$:

$$\pi + \omega = \frac{p_o}{\rho_{vo}} \ln \frac{p}{p_o} \qquad (D_1)$$

These equations are general and hold for either pressure potential or osmotic potential or both. The addition of air into the system would increase the pressure throughout by a constant amount. But since the value of π is defined as zero at the free flat surface of the liquid the pressure potentials referred to that surface as zero would remain the same. The other potentials would not be affected.

Calculation of forces. By using formula (D_1) the forces set up between a dry soil and pure water can be calculated. As was shown in table 3, a difference of 0.34°C. in temperature between the soil and water would cause the soil to dry out to 98 per cent of its maximum vapor pressure. If the water is 25.0°C. its vapor pressure would be 2.378 cm. of mercury, and since the soil is in equilibrium with this water, its vapor pressure, p, would be the same. As previousy stated this would be 98 per cent of its maximum vapor pressure, p_o, which would be 2.427 cm. The density of this vapor, ρ_{vo}, would be 0.000,023,50 gm. per cc. Then by (D_1), since the pressures must be reduced to dynes per square centimeter:

$$\pi + \omega = \frac{2.427 \times 13.6 \times 980}{0.000,023,50} \ln \frac{2.378 \times 13.6 \times 980}{2.427 \times 13.6 \times 980}$$

$$= -27,819,900 \text{ dyne-cm./gm.}$$
$$= -28,381{,}1 \text{ gm.-cm./gm.}$$
$$\pi + \omega = -27.46 \text{ cc.-atm./gm.}$$

Since in a washed soil the osmotic potential, ω, is practically zero the value calculated above is the pressure potential, π. If this soil is 10 cm. from the water and is connected by a wick there would be an average net force of $\frac{28,381}{10}$ = 2,838.1 gm. for each gram of water in the wick driving it from the water to the soil. From this it is evident that ordinary laboratory light is enough to cause serious departures from mechanical equilibrium.

The effect of different temperatures on equilibria

By the use of potentials some of the temperature effects on absorption of vapor, reported by various workers under different conditions can be explained. For instance Hilgard (3) reports that the "hygroscopic coefficient" increases

with the temperature, whereas Patten and Gallagher (5) report that the amount of water vapor absorbed by a soil from a saturated atmosphere decreases as the temperature rises. These experiments were carried out under widely different conditions. Hilgard placed his soils in boxes lined with wet blotters. These were kept in a cellar, where any temperature fluctuations would be very slow. Inside of a wood box the effect of light would be almost negligible, but since in his experiments he allowed only 8 hours for absorption, equilibrium would not have been reached. This is evident from the fact that in the absorption experiments carried out by the author equilibrium had not been reached after 56 days. Since, in Hilgard's experiments, equilibrium had not been reached, the more available the water vapor was made to the soil the faster it would absorb it, and since the rate of diffusion of water vapor increases rapidly with the temperature, the higher the temperature the faster would be the diffusion of vapor to the soils and the more they would absorb in a limited time.

In contrast to this, Patten and Gallagher allowed enough time for equilibrium to be reached but they had the soils in desiccators in a thermostat heated with incandescent lamps and as a result the soils were at a higher temperature than the solutions in the bottom of the desiccator. The result would be that the soils would come to vapor equilibrium at a dryer point than if there were no light. At isothermal equilibrium the total potential of the soil and solution must be the same, for if not and if the soil and solution were connected by suitable wick there would be a motion of water. When it is remembered that the drier the soil the more negative the pressure potential, it can be seen that when soil first in isothermal equilibrium with a solution is exposed to light, the resultant drying will make the potential of the soil less than that of the solution. Thus there is a positive heat of transference from the solution to the soil. This heat of transference is positive since the potential of the soil is less than of the solution, which means that work will be done by the water in transferring itself from the solution to the soil and thus heat will be given off. By Le Chatlier's theorem of mobile equilibrium, if the temperature of the system is changed the equilibrium will be displaced in such a way as to diminish the change in temperature. This tendency to cool if the system is heated will be accomplished by distillation of water from the soil to the solution, so if the temperature is increased the soil will dry.

If in either case an isothermal equilibrium had been reached the potential of the soil and of the solution would have been the same, so there could have been no heat of transference of water in either direction. By the above theorem a change in temperature would in no way affect the equilibrium point.

Another effect would tend to increase the error made by Patten and Gallagher. At higher temperatures more heat would be required in the thermostat and thus there would be more light and a greater resultant drying.

The detailed discussion of potentials and of their relation to vapor pressure has been useful in calculating mechanical stresses caused by light, the driving

forces in soil moisture, and has given a method of determining the effect of temperature on equilibria. This latter shows that in at least the above two cases cited, the experimental results show that the workers had not reached the "hygroscopic coefficient" as they had defined it. This strengthens the conclusion previously reached that soil cannot be in isothermal equilibrium with a saturated vapor when drier than saturation.

SUMMARY

An unexpected drying out of wet soils was noted when they were placed in desiccators over water in a constant temperature bath.

Several absorption experiments were carried out in an apparatus designed so that it was possible to determine the amount of water absorbed at any time without opening the desiccator or removing it from the bath.

The amount of water absorbed from a saturated atmosphere when the desiccator was kept dark exceeded twice the so-called "hygroscopic coefficient." When a beam of light was turned into the desiccator all the soils dried out to a moisture content equivalent to about 84 per cent of their maximum vapor pressures. When the lights were turned off the soils began to absorb moisture again, showing that light absorbed by the soil caused the drying out noted.

A thermocouple was used to measure the difference in temperature between a soil and water in a submerged desiccator. The difference was found to be 4.5°C. when a 300 c.p. light with a reflector 50 cm. away was used, 0.5°C. when the reflector was removed, 0.16°C. due to the laboratory light during the day and within the experimental error at night.

To make sure that there could be no isothermal equilibrium between relatively dry soil and a saturated water vapor it was shown by geometry and mechanics that, at least for uniform spheres, such an equilibrium would be impossible.

A general discussion of potentials is given and four—the gravitational, pressure, osmotic, and total potentials—are defined. The relationship between the sum of the osmotic and pressure potentials in a liquid and the equilibrium vapor pressure is derived.

The forces that exist between wet and dry soils in contact are shown to be enormous, by calculating the pressure potentials from vapor pressure data. The relationship between these two functions is derived.

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